LOW TEMPERATURE CARBONIZATION OF NON-CAKING COALS & LIGNITES AND BRIQUETTING OF COAL FINES

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L.T.C. Vol. II

The industrial application of low temperature carbonization (l.t.c.) of coal has been restricted to only a few countries to meet special needs although the concept of l.t.c. is more than a century old. However, it is now gaining importance as a method of utilization of weakly caking, non-caking and low grade coals and lignites which are available in abundance compared to the limited reserves of high grade coking coals. This has added significance to India, where there is an urgent need for providing smokeless domestic fuel to the vast population in the country as a substitute for firewood, charcoal and dung. The tar obtained could form an important raw material for development of chemical industry in the country.

The Regional Research Laboratory, Hyderabad, organized a symposium on low temperature carbonization of coal during November 20–22, 1961 to review the progress of research and technological developments in the field and project the future plan of work. A wide cross-section of research scientists, coal technologists and industrialists and representatives from several leading coal producing firms in West Germany, and U.K. participated in the deliberations.

In the first volume, papers and discussions relating to the first two sections of the symposium, viz. Briquetting of Non-caking Coal Fines, and Low Temperature Carbonization of Non-caking Coals and Lignites, were included. In the present volume, papers and discussions relating to the remaining two sections, viz. Products of Low Temperature Carbonization, and Survey, Economics and Statistics of l.t.c. Products, are presented.

The publication will be useful to all those interested in research and development of low temperature carbonization industry and its byproduct utilization.

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Symposium Organized By

The Regional Research Laboratory, Hyderabad
November 20-22, 1961

(In Two Volumes)

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SECTION THREE

Products of Low Temperature Carbonization

Laboratory Investigations on the Briquetting of Upgraded Salem Iron Ore, Neyveli Char and Lime Using 'Viscolex' as a Binder

C. V. S. RATNAM & A. RAJENDRAN

Neyveli Lignite Corporation
Neyveli

Laboratory investigations on briquetting of beneficiated Salem iron ore with char from South Arcot lignite and calcium oxide have shown that 6 per cent of 'Viscolex' binder can produce good and strong briquettes. Particle size, concentration of ingredients, time of curing and temperature of curing affect the strength of briquettes. It is shown that the strength of briquettes can be improved by aging, curing in a stream of flue gases or by heating in an air oven.

India is on the threshold of great developments in the iron and steel industry. The targets for production of steel during the Second and Third Five Year Plans have been fixed at 6 million and 10 million tons per annum respectively. In the Fourth Plan the target is likely to be about 20 million tons.

Though India is relatively rich in iron ores, she is not adequately endowed with coking coals, essential for production of iron and steel in conventional blast furnaces. The reserves of coking coal in India are estimated to be only 700 to 750 million tons out of the total coal reserves of 20,000 million tons[1]. These coking coal reserves are not evenly distributed all over the country, but are concentrated in the Bengal-Bihar region. Moreover, there are certain areas in the country where large reserves of good quality iron ores are available, but these areas do not have any coking coal reserves. Thus for the growing needs of iron and steel industry and for a rational distribution of the industry throughout the country, it may be necessary to use noncoking coals for iron ore reduction. A case in point is the availability of large reserves of iron ore in the Salem district of Madras State and the availability of lignite[1], at nearby Neyveli which is only 90 miles from the iron ore reserves at Salem. If an iron and steel industry is to be established in Madras State, it can only be based on the lignite at Neyveli.

There are a large number of methods for the reduction of iron ores using noncoking coals[2]. One of these methods is to briquette powdered iron ore and the reducing agent and use these briquettes as feed into a low shaft furnace or even in a blast furnace. The iron ore at Salem is magnetite with about 35-37 per cent iron. Work has already been done on beneficiation of these magnetites by magnetic separation[3]. It has also been proved that lignite char obtained from the South Arcot lignite can be used as a reducing agent. This paper describes the investigations carried out to see whether good quality briquettes of ore, reducing agent and flux could be produced by using a suitable binder. Of the various binders tried, 'Viscolex', a colloidal compound containing lignosulphonates was found to be very promising.

EXPERIMENTAL PROCEDURE

Materials

(1) Salem iron ore, crushed to 80 mesh and beneficiated in Dings Wet Magnetic Separator;
(2) Char produced by carbonization of Neyveli lignite briquettes;
(3) Calcium oxide, essential as flux; and
(4) 'Viscolex', a waste product from pulp and paper industry (sulphate process), to be used as binder.

A briquetting and carbonization plant with a capacity of 380,000 tons of carbonized briquettes per annum is now under erection at Neyveli. This plant is expected to produce considerable amounts of char fines which cannot be disposed of as a domestic fuel. These could be used for reduction of iron ores. The fines used in this investigation are similar to those that can be expected from the commercial plant. 'Viscolex' consists principally of lignin compounds and is a free-flowing solid, easily soluble in water and can easily be mixed as a binder. Although not at present being produced in India, it can, however, be produced in some of the paper mills in the country, if there is enough demand for the product.

The crushed and beneficiated Salem iron ore was mixed with sized lignite char, calcium oxide and 'Viscolex'. The whole mass was mixed thoroughly and made into briquettes of 50 mm. diam. with the help of a universal testing machine at a briquetting pressure of 1000 kg./sq. cm.

RESULTS AND DISCUSSION

Table 1 gives the chemical analysis of Salem iron ore and the beneficiated product obtained from it. Table 2 gives proximate analysis of the lignite char fines. The results of recovery of magnetite from Salem iron ore by the magnetic beneficiation are plotted in Fig. 1. It can be seen that the difference in the recovery of ore between crushing to below 40 and 80 mesh is not more than 6 per cent. In Fig. 2 the data showing the relationship between strength of the briquettes and particle size of the beneficiated ore have been plotted. There is some increase in the strength of briquettes with a decrease in particle size of the ore. However, the strength of briquettes using the material of 40 mesh size is quite high (of the order of 100 kg./sq. cm.) and it may not be necessary to decrease further the size of ore particles involving high cost of power.

The influence of percentage of binder and period of curing on the strength of briquettes is shown in Fig. 3. Several compositions of the ore, reducing agent, flux and binder were used. It is clear from Fig. 3 that in every case there was considerable increase in the strength of briquettes with increase in the period of curing. Even with a mixture containing only 6 per cent binder, a considerable ultimate strength of 126 kg./sq. cm. was obtained.

TABLE 1—CHEMICAL ANALYSIS OF SALEM IRON ORE

	%		%
SiO_2	44.44	S	0·002
Al_2O_3	..	P	0·136
Fe_2O_3	42·15	Loss on ignition	0·65
CaO	..	Fe	37·86
MgO	..	Recovery of concentrate by weight	80·0
		Iron content of concentrate	64·0

TABLE 2—PROXIMATE ANALYSIS OF LIGNITE CHAR

(Temp. of carbonization, 600°C.)

Moisture, %	1·5
Ash, %	11·9
Volatile matter, %	16·0
Fixed carbon, %	70·6
Calorific value, kcal./kg.	6900

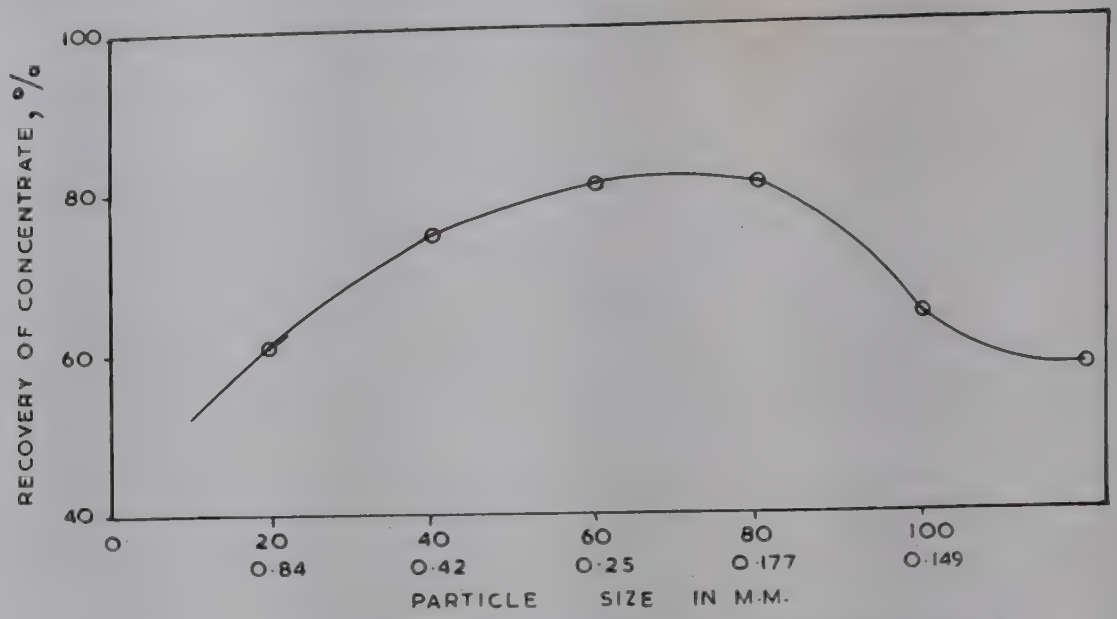

FIG. 1—PERCENTAGE RECOVERY OF IRON ORE IN DINGS MAGNETIC SEPARATOR

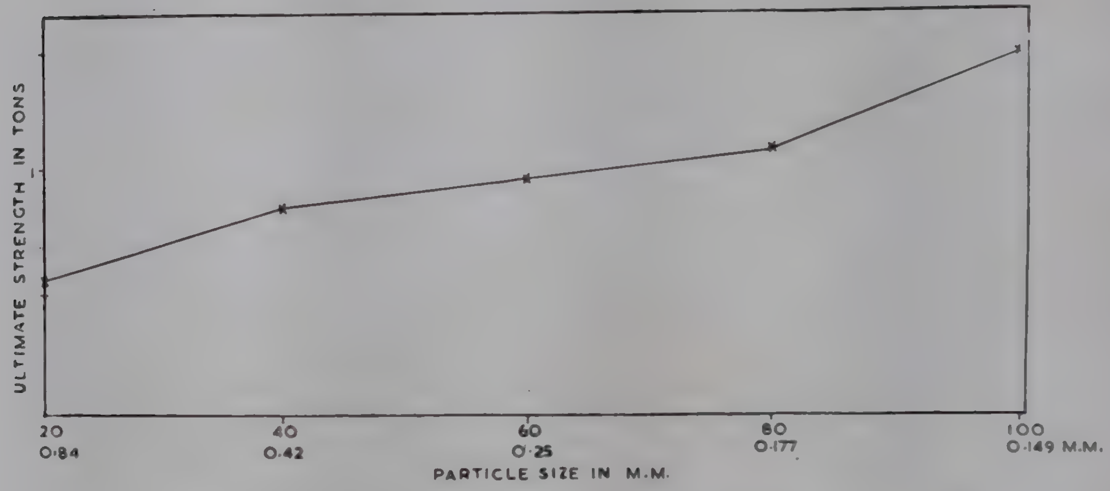

FIG. 2—INFLUENCE OF PARTICLE SIZE ON THE STRENGTH OF BRIQUETTE

In order to increase quickly the strength of the briquettes, other methods of curing were tried. Briquettes immediately after preparation, were exposed to flue gases. Action of heat on briquettes was also studied. Table 3 gives the data comparing the strength of raw briquettes, briquettes dried in an air oven at 120°C. for 30 min., and briquettes cured in flue gases at 120°C. also for a period of 30 min. It can be seen that the briquettes cured in flue gases showed greater improvements in their compression strength than those kept in the air oven. In actual practice, curing in flue gases is likely to be quite practical. The improvement obtainable in strength of briquettes by curing for a period of about 10 days can be achieved by curing the briquettes in flue gases merely for 30 minutes. When flue gases are passed over the briquettes, carbon dioxide in the gas might be reacting with the calcium oxide and binder imparting strength to the briquettes.

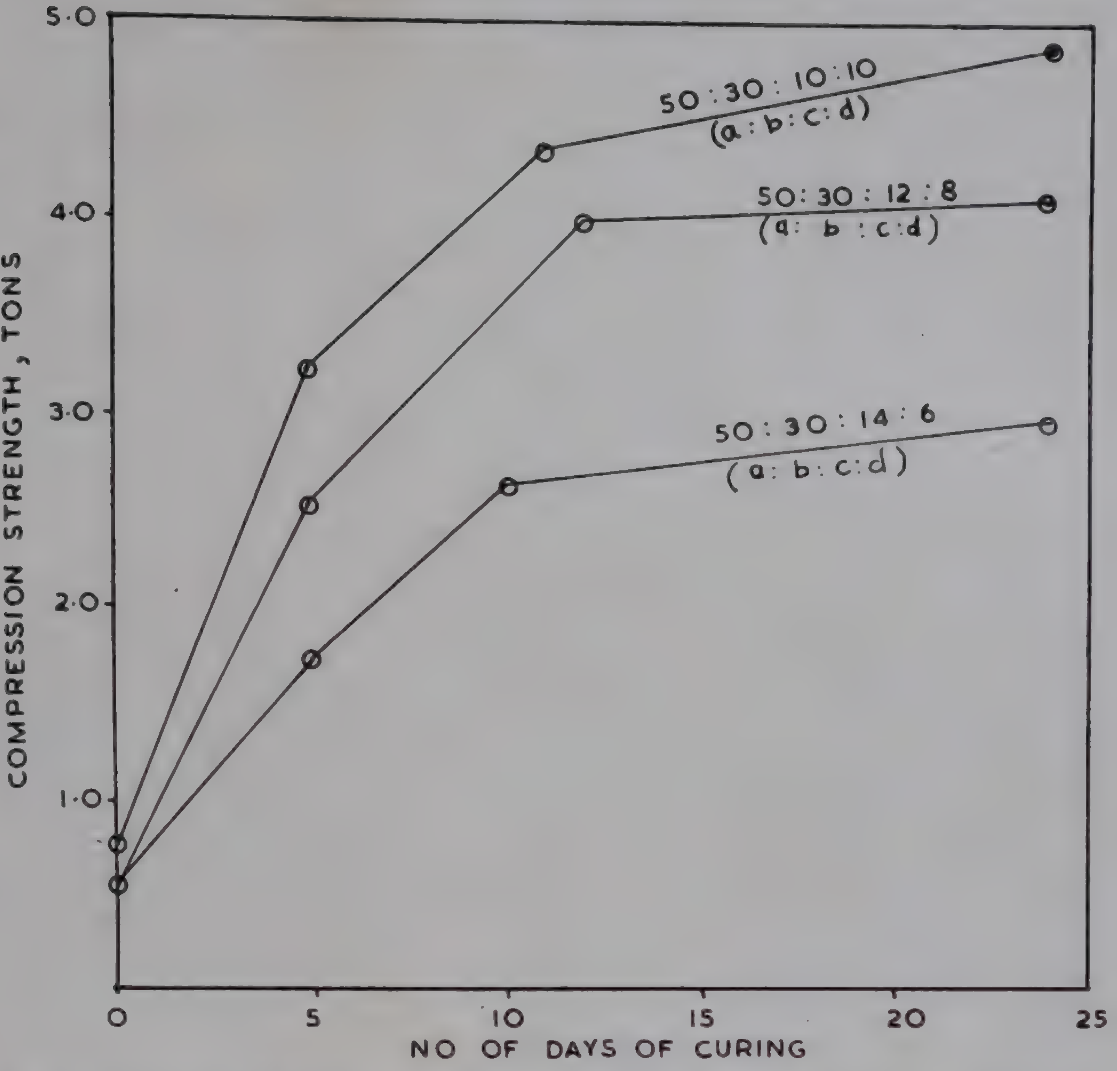

FIG. 3—INFLUENCE OF BINDER AND PERIOD OF CURING ON THE STRENGTH OF BRIQUETTE: (a) iron ore (b) char (c) lime (d) viscolex binder

TABLE 3—COMPARATIVE STRENGTH OF BRIQUETTES : RAW, AIR OVEN DRIED AND FLUE GAS DRIED

COMPRESSION STRENGTH, kg./sq. cm.		
Raw briquettes	Dried in air oven	Dried in flue gas
17·5	72·0	118·0
19·6	73·6	105·0
27·6	73·6	102·5
22·6	68·0	67·6

Further investigations are in progress to achieve optimum conditions for briquetting and curing and the smelting of these briquettes.

ACKNOWLEDGEMENT

The authors express their sincere thanks to the authorities of the Neyveli Lignite Corporation, for permitting the presentation of this paper, and to Shri T. M. S. Mani, Managing Director and to Shri A. Srinivasan, Deputy General Manager (Technical and Works) for their keen interest and encouragement.

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4. Ratnam, C. V. S. & Balachandran, T. R., *Indian Mining J., Sp. No.*, **5** (1957), 255.

DISCUSSION

Shri D. P. Agrawal: It is known that lime and sulfite liquor set to a hard mass resulting in increased strength on storage. In the present studies lime alone when used as flux has resulted in poor strength. It is likely that in combination with viscolex, lime serves both as a flux and as a binder which increases strength. I would like to know whether any experiments have been done with viscolex alone.

Dr C. V. S. Ratnam: We have in the beginning used only lime and the strength was not so good as when lime and viscolex were used together. Viscolex alone has not been tried. In briquettes of this type, lime is always to advantage. So it is not a serious problem.

Utilization of Low Temperature Carbonization Char in Coking Blends

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Possibilities of producing metallurgical coke by blending suitable lean components (carbonaceous) with high volatile caking coals are indicated and in a few cases low temperature char has been found to be a better blending component than low volatile coals. The amount of low temperature char in the blend can vary from 10-30 per cent depending upon the nature of high volatile coal. High volatile Dishergarh coals of Raniganj coalfield can be blended with 15 per cent of char from the same coal or other coals to produce a coke meeting the specifications. Low temperature char produced in rotary retorts with 15 per cent volatile matter appears to give optimum results. This method of utilization of low temperature char may help to conserve the limited reserves of good quality coking coals.

In the metamorphic series of bituminous coals the best caking and coking coals occupy different positions, the former being less mature than the latter. The best caking coals (fat coals) are marked by very highly swollen coke-button in the volatile matter test, high fluidity of the plastic state, high thickness of plastic layer, high caking index and high values of various other laboratory indices for the caking properties of coal. The best coking coals are characterized by the properties of yielding strong and hard coke on high temperature carbonization in commercial coke ovens. The coke produced by the carbonization of the caking coals is often weak and foamy and its properties can be remarkably improved by blending the coal with some lean components (carbonaceous) prior to carbonization. Low temperature carbonization (l.t.c.) char is one of such lean components notable for improving the coking properties of not only the caking coals, but also some high volatile, good caking gas coals.

The use of l.t. char (semicoke) may be traced back to as early as 1909 when Dr Shimomura of Japan discovered that the properties of coke could be appreciably improved by blending semicoke with high volatile caking coals. This discovery was of great significance particularly for Japan which, devoid of reserves of coking coals, was using 30-40 per cent of imported low volatile good coking coals in coke-oven charges. Since then considerable work[1,2] has been done in Japan in the field of utilization of semicoke in the production of blast furnace coke. An l.t.c. plant was installed in 1935 which produced semicoke with 20 per cent volatile matter from noncoking coals. This semicoke, on blending to the extent of 15 per cent with high volatile Yubari coal, led to an increase in Drum Index of the coke by 5 units (Japanese Industrial Standard). After studying the various technological factors involved, it was found that a normal blast furnace coke could be produced from a high volatile caking coal if the latter was blended with semicoke (minus 0·3 mm. size) in the ratio, coal : semicoke =20-25 : 80-75. However, these findings did not evolve a practice which could economically compete with the use of imported good coking coals from abroad.

The novel work initiated in Japan drew considerable attention in many other countries. In the present paper some of the results obtained in U.S.S.R. and India are discussed.

Panchenko[3] observed that the char with a volatile matter of 9-13 per cent obtained in rotating retorts from the Chelyabin brown coal (V.M.= 46·5 per cent d.a.f.) might serve as a lean component with fat coals. The blend consisted of 15-25 per cent char and 15-20 per cent lean caking coal. The Kizelov fat coal with these components produced a coke with a Sundgren Drum Index of 270-298 kg. (Specification[4] for blast furnace coke from Donbass coals—337 kg.). When the Kizelov fat coal was substituted by the Polovinkov fat coal, the coke produced had better physical properties (Drum Index=322/337 kg.). On using Gubakhin coal as the fat component intermediate results were obtained; the coke had a Drum Index of 280-320 kg. By omitting the lean caking coal and using the brown-coal char to the extent of 20 per cent, good cokes were obtained from all the three fat coals (Drum Index was 311-325 kg.). However, the coke pieces were of small size and the appearance of the coke mass showed that the quantity of the lean component (char) in the blend was not enough. By raising its content up to 25 per cent, a somewhat better coke was obtained, but the size was not large. A more porous and larger coke was produced when 30 per cent char was used. However, the hardness of coke decreased; the Drum Index varied from 295 to 313 kg. Increasing the char content from 30 to 40 per cent decreased both the size and hardness of the resultant coke.

In another series of experiments Panchenko prepared brown coal chars with different volatile matter contents (3 to 18 per cent d.a.f.) in a shaft-type l.t.c. oven and mixed them (up to 20-25 per cent) with the three

TABLE 1—EFFECT OF VOLATILE MATTER CONTENT OF CHAR ON THE STRENGTH OF COKE

VOLATILE MATTER OF SEMICOKE, % (d.a.f.)	DRUM INDEX OF COKE, kg.		
	Kizelov coal	Polovinkov coal	Gubakhin coal (V.M.=40%, d.a.f.)
14-18	325	315	318
9-12	297	297	298
6- 9	226	243	251
5- 6	126	208	240
Approx. 3	..	..	178

fat coals. Carbonization was done in 4 ovens and the average strength of the cokes produced was noted. The results are shown in Table 1.

It is to be seen that the increase in the degree of carbonization of the char leads to a sharp fall in the hardness of coke. The hardest coke is produced by adding to the blend a char of 14-18 per cent volatile matter. But, if the latter figure is higher, the coke strength again deteriorates (not shown in Table 1).

Another interesting observation of Panchenko was that if the carbonization was done more uniformly, the optimum degree of carbonization of the char could be raised. Thus with a char of 12 per cent V.M. obtained in a rotating retort, the Drum Index of the coke was found to be 323 kg. (as against 297 kg. with the char of 12 per cent V. M. yield, obtained in the shaft-oven).

While Panchenko studied the effect of addition of brown coal char as a lean component to highly caking fat coals, Ryabukho[5] blended high volatile caking coals (V.M.=45·55 and 47·94 per cent d.a.f.), with their own char and examined the properties of the coke produced. The chars were produced by carbonizing the coals at 550°C. for different periods. It was found that with a decrease in the V.M. of char up to a certain value (14·4 per cent) the hardness and size of coke both improved, and if the V.M. yield was decreased still further (12·77 per cent), both these properties of the coke deteriorated.

Ryabukho confirmed the findings of earlier workers that the quality of coke depends on the grain size of component (coal and char). The bigger the size of the char the worse is the quality of coke obtained. Best results were obtained when the coal was ground to −3 mm. and the char to −1 mm.

The work of Taits and Fridman[6] on laboratory and pilot plant scales showed the possibility of using l.t.c. char made from peat in coking blends. In fact, when a lean caking coal was substituted by peat char in a coking charge, coke of improved quality was obtained. At present there are a number of projects for using peat char in the production of metallurgical coke in the north-western regions of U.S.S.R.

Vaisberg[7] has discussed economics of the methods of coke making from blends containing char. The cost of installation of l.t.c. plant may be compensated by the saving in mining long flame coals instead of lean caking coals occurring at great depth. Fat coals are abundant in the U.S.S.R. They require lean components for making coke-oven charges. L.t.c. char is a prospective substitute for the lean caking coals. Long flame coals are quite suited for the production of l.t.c. char, at the same time producing tar in high yields. It is, therefore, desirable to intensify research on utilization of l.t.c. char in coking blends.

Working with American coals, Price and Woody[8] observed that all coal blends (of high and low volatile coals) yield cokes with increased shatter index and decreased Tumbler Index compared with coke from the high volatile coals alone. But when low volatile coals were substituted by l.t.c. char, both the indices improved. This shows the advantage of using char as the lean component in coking blends.

Work on Indian coals, while confirming the findings of earlier investigations, has supplied valuable information in widening the country's raw material base for production of metallurgical coke. Das Gupta and co-workers[9,10] studied the physical properties of coke obtained from blends of high volatile coals with char prepared in rotary type Fischer Assay apparatus at 500°C. from noncoking, poorly coking and good coking coals. They concluded that suitable chars of uniform composition are, in general, good blending agents irrespective of the nature of the original coals from which chars are made. However, chars from high volatile caking coals seem to be the most suitable for the purpose (Fig. 1).

High volatile and other types of Indian coals are invariably much inferior in caking properties to the corresponding high volatile coals of Europe and America. One of the reasons for this is the high mineral matter content of Indian coals. It is, therefore, understandable why Das Gupta and co-workers found 15 per cent as the optimum amount of char in the blends with Dishergarh coals (the highest caking high volatile coals of India), while some of the fat coals of U.S.S.R. could consume as high as 30 per cent of the char.

Although the nature of the original coal from which chars are made does not have big effect on the quality of coke from the blends, other properties of the char have to be carefully taken into account. For instance, Das Gupta and others noticed that the optimum range of volatile matter of the air-dried char was 11-15 per cent.

Confirming the results obtained in other countries, the same workers report that char obtained in a rotary type Fischer retort is better suited as a blending agent than that obtained in a Lurgi-Spuelgas pilot plant operating at Hyderabad. More uniform carbonization in the former equipment may be responsible for the superiority of the char made in it.

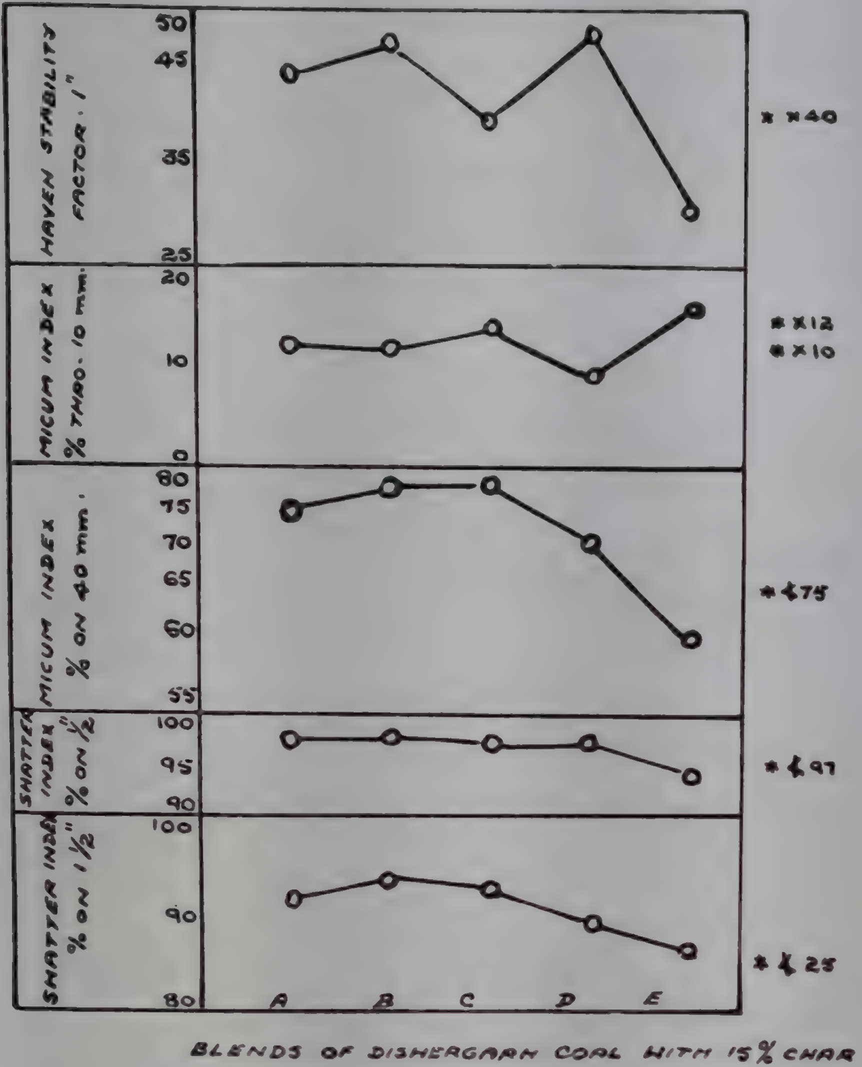

FIG. 1—EFFECT OF NATURE OF COAL USED FOR MAKING CHAR (SPECIFIED LIMIT FOR METALLURGICAL COKE) (A) from weakly coking coal (B) from poorly coking coal (C) from noncoking coal (D) from good coking coal (E) from natural coke

In addition to the good coking coals of Jharia and Giridih and medium volatile coking coals of Raniganj, India possesses reserves of high volatile caking coals mostly in the Raniganj area and also in Madhya Pradesh. The present *in situ* reserves of the Dishergarh and Sanctoria-Poniati seams in Raniganj are of the order of 400 million tons up to a depth of 2000 ft. The high volatile caking coals of these seams when carbonized alone produce weak, fingery and highly fissured coke showing physical properties much below the specified standard for metallurgical coke. Finer grinding does not generally show any appreciable improvement in the coke quality. As anticipated, addition of leaner components to the coking charge of these coals lead to a remarkable improvement in the hardness of resultant coke. Thus metallurgical coke could be produced from the following blends:

1. Dishergarh coal, 40-50 per cent; normal Jharia coal (25-30 per cent V.M., air-dried), 50-60 per cent.

2. Dishergarh coal, 80-85 per cent; specially selected low volatile good coking Jharia coal (17-23 per cent V.M., air-dried), 15-20 per cent.

It was noted that out of the two types of Jharia coals the leaner ones are more effective as blending components with the Dishergarh coal which is in conformity with what has been discussed in the earlier part of the paper. The essential role played by Jharia coals is that of a lean component to the high volatile Dishergarh coal. Thus the low volatile Jharia coals could be entirely substituted by l.t.c. char. The coke obtained from a blend of 85 per cent Dishergarh coal and 15 per cent char produced from the same Dishergarh coal or any other coal had the following physical properties: Shatter index on 1·5 in., 92·3; Micum index on 40 mm., 77·1; Haven stability factor on 1 in., 43·4, while the corresponding indices of coke from 100 per cent Dishergarh coal were 72·46 and 17.

The significance of the results is far-reaching. It is possible to resort to an effective conservation of the limited reserve of the upper seam Jharia coals. It is also feasible to feed the Durgapur Steel Plant with coke from coal drawn solely from the Dishergarh or similar seams. Finally, this good outlet for the char lends support to the establishment of l.t.c. industries in India.

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A New Process for the Utilization of Non-caking Coal Chars as Domestic Fuel and as Metallurgical Coke

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A process has been developed for the utilization of chars from low-rank coals as domestic fuel and metallurgical coke. It comprises of mixing sized fractions of char with suitable inorganic binder (taking care to see that ash in the final product does not exceed that stipulated for metallurgical coke) and moulding into required shape. High temperature chars from South Arcot lignite, Poniati, Samla and Jambad-Bowlah coals and low temperature coke were tested by this process for Shatter and Haven indices. An inorganic binder was used as such or blended with suitable proportion of pozzulonic material. Low temperature coke breeze can be successfully moulded into convenient shapes using 8 per cent binder or 10 per cent of a mixture of binder and pozzulona and the shapes have very high Shatter and Haven indices. The Haven index can be improved by addition of sodium silicate, bentonite or calcium chloride. The shapes from low temperature coke breeze burn well in a domestic 'chula' and do not disintegrate in water.

At present nearly 30 per cent of coal as mined is of 0-1 in. size. With increase in mechanization the amount of slack coal would further increase. At present most of these fines do not find any use and are wasted. Fluidized carbonization of the fines would yield a reactive char which, after briquetting, can be used as domestic fuel. Similarly, during the low temperature carbonization (l.t.c.) of coal in the conventional process nearly 10-15 per cent of the product is in the form of fines, which do not find suitable use. From the coke-oven plant also, considerable amount of coke breeze is produced.

TABLE 1—PROXIMATE ANALYSIS OF RAW MATERIALS AND MOULDED SHAPES

(Air-dried basis)

Nature	Binder %	Moisture %	Ash %	Volatile matter %	Fixed carbon %
South Arcot lignite char (1000°C.)	..	1·0	16·1	4·1	78·8
South Arcot lignite char shapes	10·0	9·8	24·2	6·6	59·4
Jambad-Bowlah char (1000°C.)	..	2·4	14·2	1·3	82·1
Jambad-Bowlah char shapes	7·7	3·0	20·1	4·5	72·4
Samla char (1000°C.)	..	1·6	18·0	1·9	78·5
Samla char shapes	7·7	2·0	23·1	4·5	70·4
Poniati char (1000°C.)	..	2·3	19·5	2·4	75·8
Poniati char shapes	6·25	5·8	23·4	4·7	66·2
L.T. breeze	..	6·3 5·7	33·9 35·3	4·6 5·2	55·2 53·8
L.T. breeze shapes	10·0	6·8	39·3	6·5	47·4
do	7·7	8·6	37·5	10·2	43·7
do	6·25	5·9	38·9	5·6	49·6
do	4·00	6·1	37 2	5·6	51·1

There is at present no satisfactory method of briquetting the coke breeze. The conventional methods make use of a binder-like pitch which is costly and produces smoke. Also these methods require elaborate briquetting plants which are not indigenously manufactured. The present paper describes a new process for the manufacture of briquettes and moulded shapes from coke breeze and the like.

MATERIALS

High temperature chars were obtained from South Arcot lignite and Samla, Jambad-Bowlah and Poniati coals by carbonizing them in sealed tins inserted in the 18 in. width oven of the high temperature carbonization (h.t.c.) plant. Table 1 presents analyses of the coke breeze and l.t. coke used in these experiments.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of three stages. In the first stage the coke breeze was separated into two suitable size fractions, 0-1/8 in. and

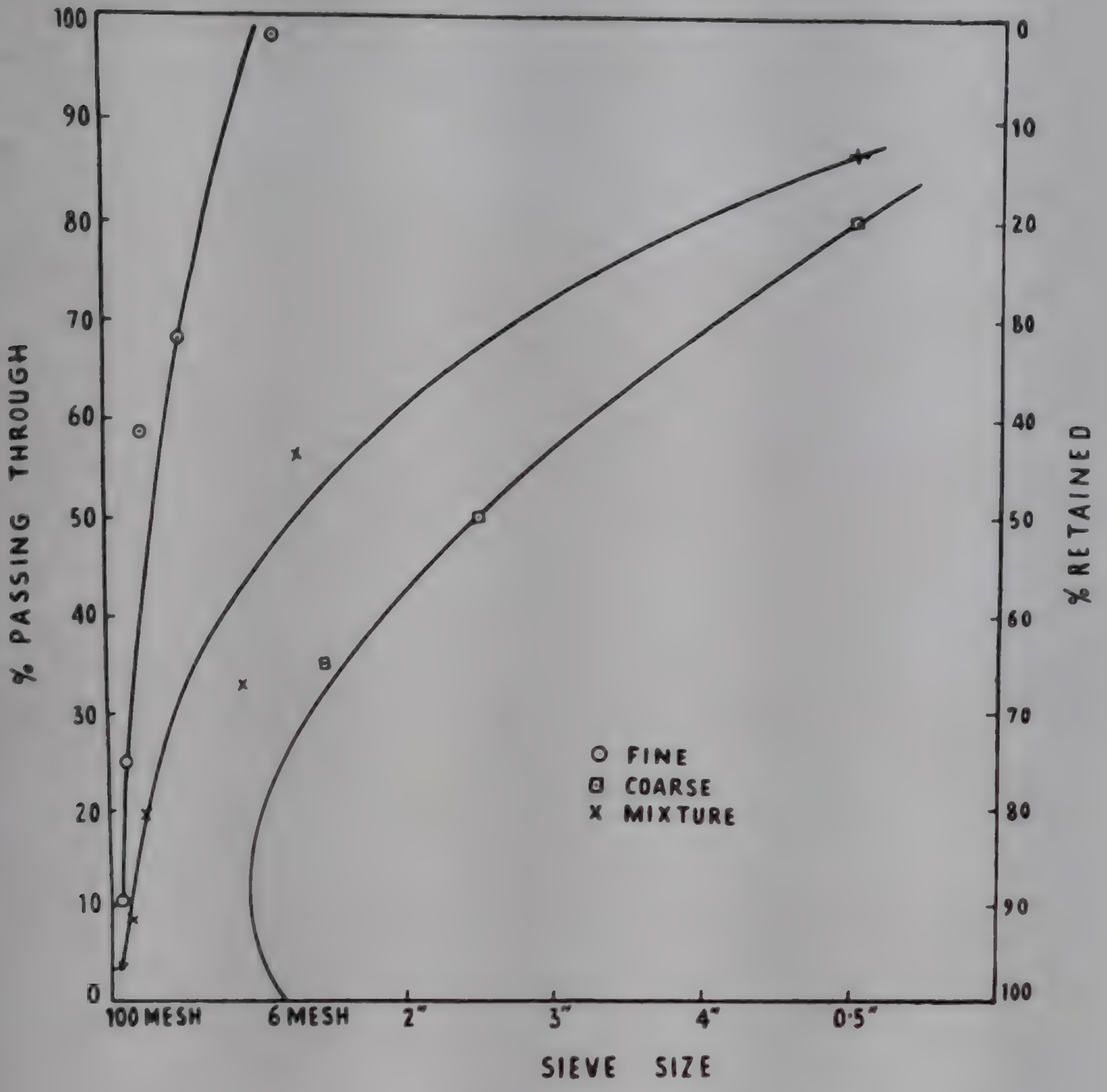

Fig. 1—Sieve analysis of coke breeze

1/8-1 in. Fig. 1 presents the sieve analysis. In the second stage, the coarse and fine aggregates were proportioned in relation to the inorganic binder ensuring a voidage range of 40-50 per cent. In the third stage, the inorganic binder admixed with the pozzulonic material or the pozzulonic material admixed with lime was added to the coke breeze. After adding proper proportion of water the mix was moulded into the required shapes. The shapes were tested for Shatter index and Haven index after suitable periods of storage. For Shatter index 5 lb. of the moulded shapes were dropped 4 times over 1/2 in. thick iron plate from a height of 6 ft and the product screened on 2 in. and 1½ in. sieves. For the Haven test 22 lb. of the shapes were tumbled in an iron drum of 36 in. diam. and 18 in. width for 200 revolutions. In the case of h.t. char the shapes were tumbled for 1500 revolutions. The products obtained in both the cases were screened through 2 in. and 1-1½ in. sieves.

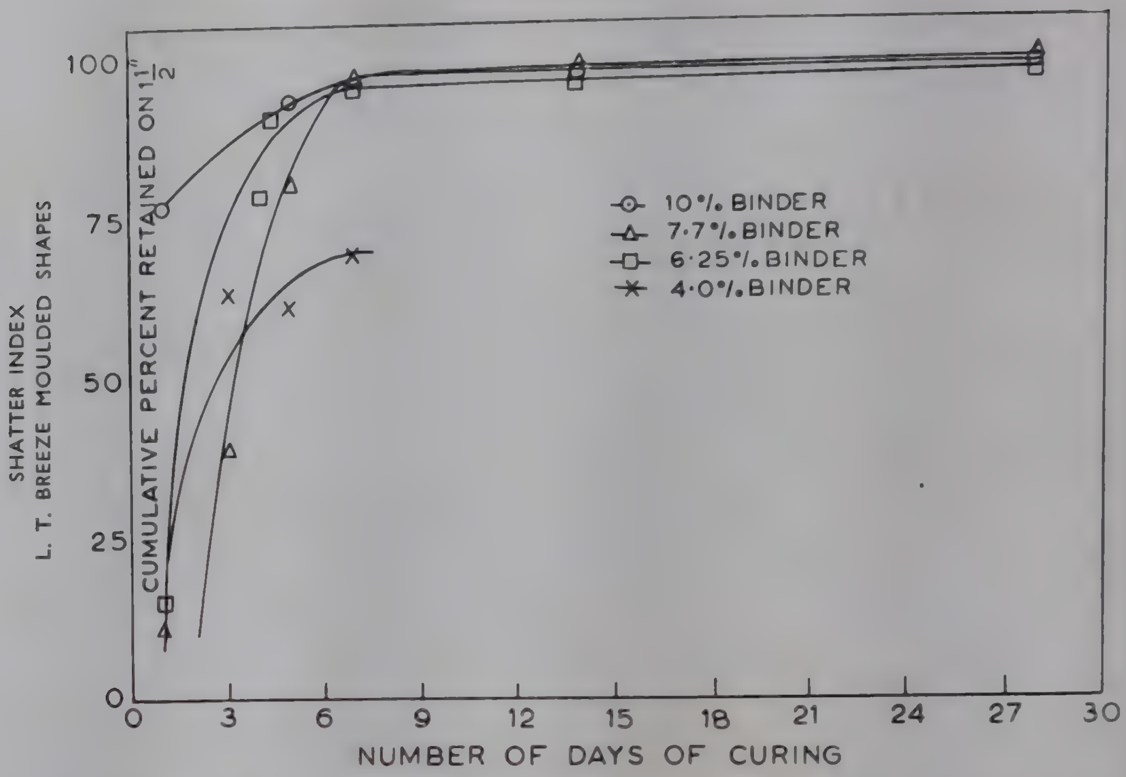

Fig. 2—Influence of curing on the shatter index of low temperature coke at different concentrations of binder

DISCUSSION

Briquetting of Low Temperature Coke. The influence of binder and the period of curing on the briquetting properties of the l.t. coke briquettes are presented graphically in Fig. 2. In general the strength of the briquette increases rapidly in the first week of storage and thereafter is not very much influenced by the period of curing. The influence of percentage of binder is prominent in the initial period (1 week). During this period, with increase in concentration of binder there is an increase in the Shatter index of the briquette. The strength of briquettes becomes almost independent of increase in concentration of binder above 6 per cent after one week's curing. It is interesting to note that even with 4 per cent binder the Shatter index obtained after 7 days curing was over 70 per cent and the Shatter index obtained under optimum conditions was over 95 per cent.

Fig. 3 is a graphical representation of the influence of binder and curing on the Haven index of the l.t. coke briquette. The Haven index increases with increase in the concentration of binder as well as its curing in the initial week.

Briquetting of L. T. Coke with Pozzulonic Binder. The results obtained by briquetting l.t. coke with different concentrations of pozzulonic binders are presented in Table 2. The Shatter index obtained after 7 days curing increases with increase in concentration of the binder and 10

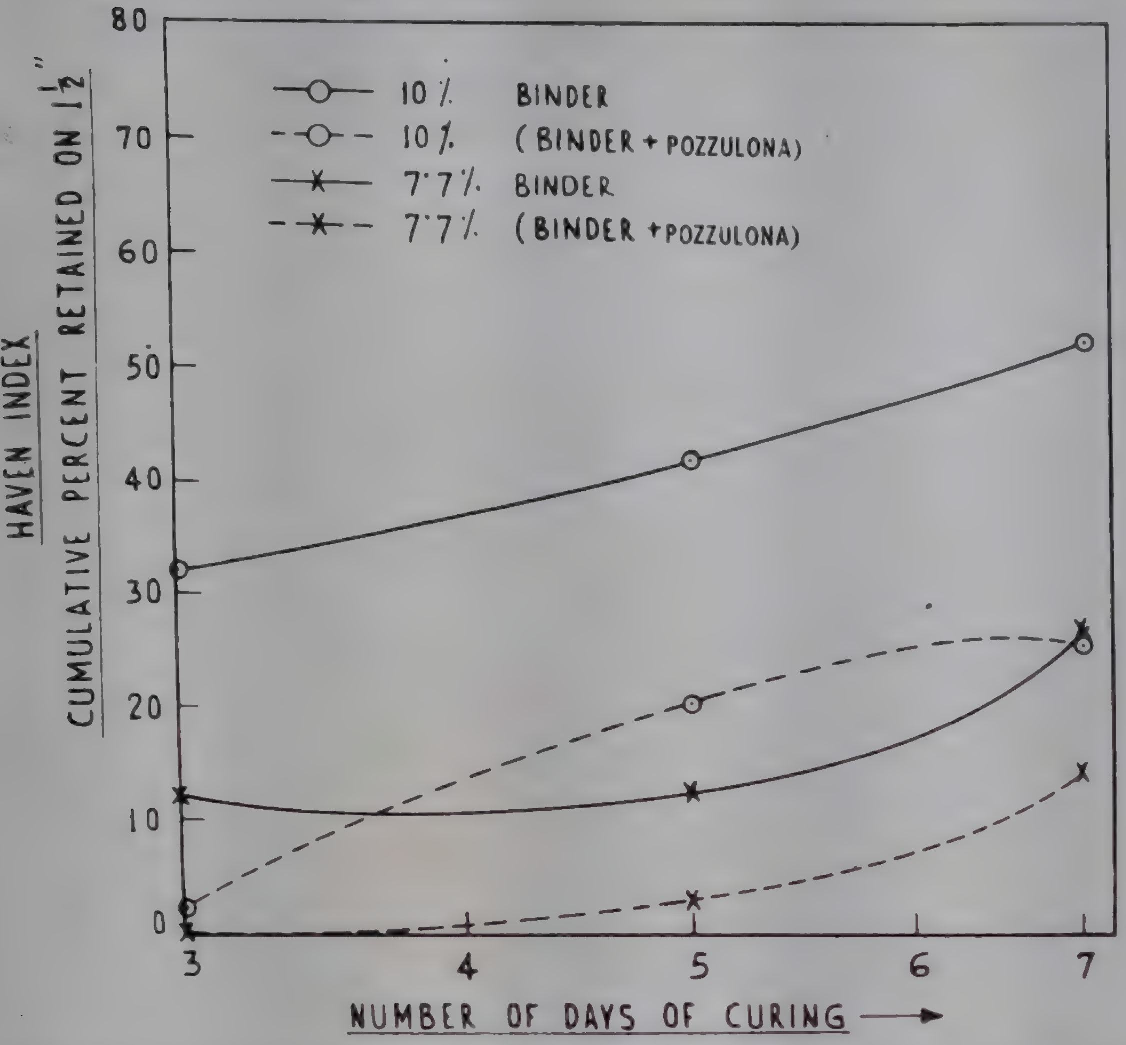

FIG. 3—INFLUENCE OF CURING ON THE HAVEN INDEX OF LOW TEMPERATURE COKE BRIQUETTE AT DIFFERENT CONCENTRATIONS OF BINDER

TABLE 2—INFLUENCE OF POZZULONIC MATERIAL ON THE STRENGTH OF THE L.T.C. BRIQUETTES

	Nature of Binder					
	Binder		Binder+Pozzulona		Pozzulonic briquettes	
Binder, %	10·0	7·7	10·0	7·7	10·0	7·7
Days of curing	7	7	7	7	7	7
Shatter index + 2 in., cum. %	97·23	97·27	86·0	69·0	93·0	83·0
Haven index (200 revolutions) + 2 in., cum. %	53·4	27·3	26·1	14·8	12·0	15·0

percent pozzulonic binder gives almost the same Shatter index as the inorganic binder. The Haven index, however, is lower.

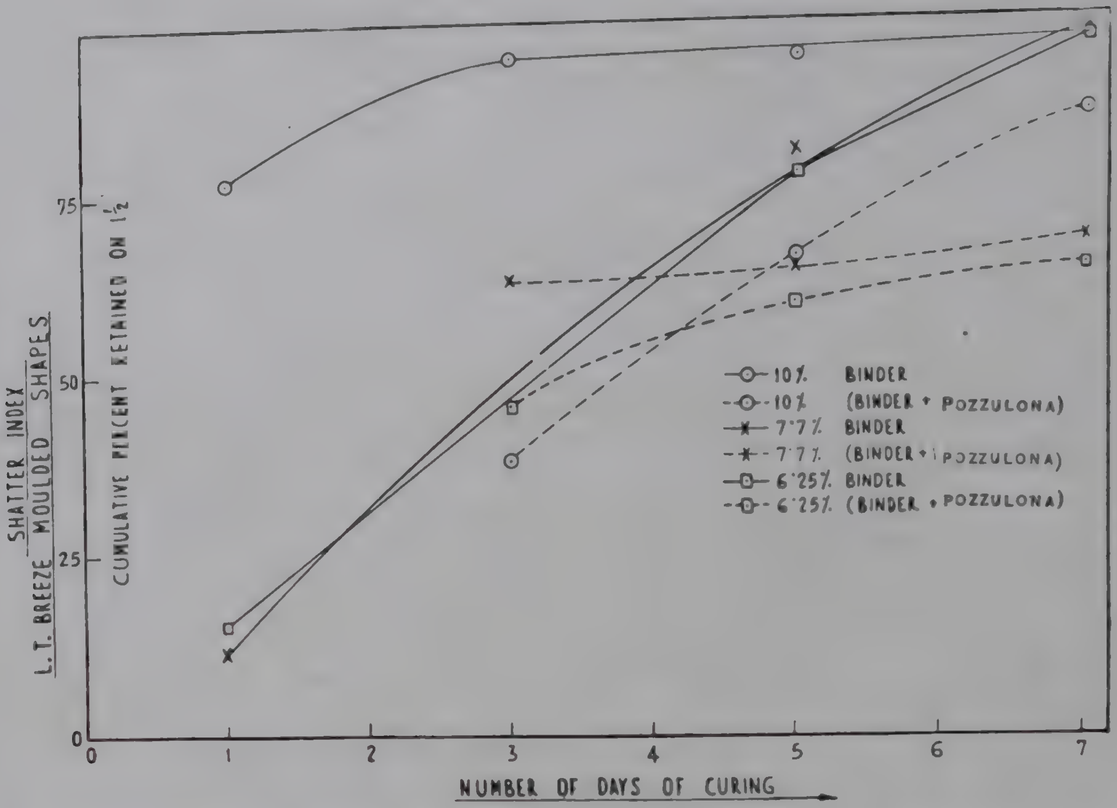

FIG. 4—INFLUENCE OF CURING ON THE SHATTER INDEX OF LOW TEMPERATURE COKE BRIQUETTE WITH DIFFERENT CONCENTRATIONS OF POZZULONIC BINDERS

The influence of admixture of pozzulonic binder with inorganic binder on the Shatter index of l.t. coke having different concentrations of binder was also studied (Fig. 4). In general, admixture of pozzulonic material to the inorganic binder gives lower Shatter index than that obtained with inorganic binder. The briquettes obtained with admixtures of inorganic binder and pozzulonic material are, however, of sufficient strength for use as domestic fuel. The Haven index of the briquettes obtained with inorganic binder is considerably improved by the addition of sodium silicate, bentonite and calcium chloride in small concentrations (5-7 per cent) as is evident from Table 3.

TABLE 3—INFLUENCE OF ADDITIVES ON STRENGTH OF L.T.C. BRIQUETTES

(% Binder=10·0; Days of curing=7)

ADDITIVE ADDED TO MIXTURE	5% Na_2SiO_3	2·5% BENTONITE	2·0% $CaCl_2$	BINDER WITHOUT ADDITIVE
Haven index (200 revolutions)				
+ 2 in., cum. %	69·44	64·8	63·6	53·4
+1½ in., cum. %	69·44	64·8	63·6	53·4

TABLE 4—H.T.C. BRIQUETTES OBTAINED FROM DIFFERENT RANK COAL CHARS AT 1000°C.

NATURE	BRIQUETTING OF CHARS								
	Poniati		South Arcot lignite		Samla		Jambad-Bowlah		Jambad-Bowlah
Inorganic binder, %	6·25		10·0		7·7		7·7		10·0+ 2% $CaCl_2$+ 2% Na_2SiO_3
Days of curing	7	14	7	14	7	14	7	14	14
Shatter index (5 lb. 4 drops)									
+2 in., cum. %	71·0	97·38	96·12	..	87·9	89·9	86·38	87·7	90·5
+1½ in., cum. %	71·0	97·38	96·12	..	87·9	89·9	86·38	87·7	90·5
Haven index, 22 lb. (1500 revolutions)									
+ 2 in., cum. %	..	11·4	..	13·0	..	9·1	..	11·4	42·1
+1½ in., cum. %	..	11·4	..	13·0	..	9·1	..	11·4	42·1

Briquetting of H. T. Chars. Experiments were also conducted to see if chars from h.t.c. of noncoking coals could be briquetted to yield shapes for use in the blast furnaces. The chars briquetted with an inorganic binder, not exceeding 10 per cent and after suitable number of days of curing the briquettes were tested for Shatter and Haven indices according to metallurgical specifications. The results obtained are presented in Table 4. It would be seen that while the Shatter index of the briquettes is very high (above 95 per cent) conforming to the metallurgical specifications, the Haven index is low. However, addition of 2 per cent each of calcium chloride and sodium silicate to 10 per cent binder gives briquettes of Haven index above 40 per cent which conforms to metallurgical specifications.

ACKNOWLEDGEMENT

Thanks are due to Shri N. N. Das Gupta, Assistant Director, Carbonization Division, for providing facilities for carrying out the physical tests, to the Analytical Section for carrying out analyses of the samples, and to the colleagues of the Briquetting Division who took part in the investigations.

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DISCUSSION

Shri D. P. Agrawal: In Bombay, charcoal and coal are briquetted into an ovoid shape called 'Badam Kolsa', using black clay as binder. A patent has been granted to Shri S. P. Bhagat for briquetting soft coke and coke breeze with cement and clay as binder. I would, therefore, like to know the new features of the process described in the paper.

Dr S. K. Sircar: Why was pozzulonic material not chosen as a binder. Calcium chloride might be objectionable for iron smelting.

Dr M. S. Iyengar: The process developed by us is different from the one mentioned by Shri Agrawal. As we have applied for a patent, we are not in a position to reveal the nature of the binder. Boiler clinker from thermal power stations, with and without grinding is used.

Calcium chloride dissolves in water during setting, and does not remain in the briquette. Hence there is no deleterious effect due to its presence.

Utilization of Low Temperature Chars for Coke Making: Effect of Blend Variables on Coke Strength

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Possibilities of improving the quality of coke from high-volatile coals of different Gieseler fluidities by blending a variety of carbonaceous inert materials, such as low temperature and high temperature chars, coke fines and finely ground noncoking coal have been investigated. Improvement in shatter strength of cokes from coals of medium or low fluidity can be explained by the reduction in volatile matter of charge. Abrasion hardness of coke was found to depend on coal charge density, swelling of blend and volatile content of additive. Density and porosity of coke were respectively proportional to charge density and to volume of voids in charge.

Swelling and volatile content of main coal ingredients were also important in determining the extent of the changes occurring in the carbonization of blends. Increase of shatter strength appears to be directly proportional to volatile matter content of basic coal and inversely proportional to its fluidity. Shatter strength of cokes from blends containing high-volatile, very highly fluid coal or medium-volatile coal of medium or high fluidity could not be improved by blending with low temperature chars.

Low temperature fluidized bed char (prepared at about 500°C. and containing about 15 per cent volatile matter) was the most beneficial for blending with a coal of high-volatile, medium fluidity and its optimum concentration was 10-15 per cent. Fine grinding was necessary to achieve firm bonding of inert particles into the cell walls of fused coke.

Blending low-volatile carbonaceous materials with high-volatile coals to improve their coking properties has been practised for more than a century. Among the materials employed for this purpose are anthracite fines[1,2], coke breeze[3,4,5], semicoke[6], and high temperature (h.t.)[7,8,9] and low temperature (l.t.) chars[10–26]. Such blending has been necessarily on empirical lines, because little was known of the complex changes occurring during carbonization of blends.

Of the six States in the Commonwealth of Australia, New South Wales (N.S.W.) has the highest annual production (20 million tons) and largest reserves (11×10^9 tons) of bituminous coal. However, only a portion of this coal (that from the Southern Coalfield) is directly suitable for the manufacture of strong metallurgical coke. Coals from the Northern Coalfield with a high-volatile content of 30-42 per cent on air-dried basis yield fissured cokes when carbonized alone, and in view of the importance of these coals as a source of metallurgical coke the Division of Coal Research, C.S.I.R.O., has carried out numerous technical-scale blending tests to study the effect of the following blend variables on the strength of the coke product:

Inert additive (*a*) Volatile Matter (V.M.) content (nature)
(*b*) Proportion in blend
(*c*) Particle size
(*d*) Porosity and shape
Basic coal (*a*) V.M. content
(*b*) Swelling (fluidity)
Blended charge (*a*) V.M. content
(*b*) Swelling (fluidity)
(*c*) Charge density (void volume)

The temperature of carbonization and the size grading of the basic coal were kept constant in the experiments, in order to simplify the analysis of the effects of blend components.

COALS AND INERT ADDITIVES USED FOR BLENDING

Properties of the blend components are given in Table 1. The three high-volatile coals which formed the main subject of the present investigation

TABLE 1—PROPERTIES OF COALS AND ADDITIVES
(Results are given as wt % unless otherwise stated)

BLEND COMPONENTS	VOLATILE CONTENT		ASH YIELD	B.S. SWELLING NUMBER	MAX. FLUIDITY IN GIESELER PLASTOMETER (dial div./min.)
	Air-dried basis	Dry ash-free basis			
COALS					
1. High-volatile, low-fluidity (Young Wallsend, St.B., Weathered)	30·8	37·3	14·1	3·5	16
2. High-volatile, medium-fluidity (Young Wallsend, St.B., fresh)	31·5	38·4	14·9	5	210

(*Contd.*)

TABLE 1—*Contd.*

Blend components	Volatile content		Ash yield	B.S. swelling number	Max. fluidity in Gieseler plastometer (dial div./min.)
	Air-dried basis	Dry ash-free basis			
3. High-volatile, high-fluidity (Fiery)	31·0	36·3	12·9	8·5	5000
4. High-volatile, medium-fluidity (Young Wallsend, Boston)	34·0	40·0	11·3	6	210
5. High-volatile, high-fluidity (Stockton Block No. 2)	35·0	35·7	0·2	9	960
6. Medium-volatile, medium-fluidity, (50-50 blend, Bulli-Wongawilli)	21·9	26·0	14·4	7	450
7. Medium-volatile, high-fluidity (Eclipse)	29·3	34·9	14·3	>9	8300
CARBONACEOUS INERT ADDITIVES					
Low Temperature Fluidized-bed Chars:					
1. From noncoking coal (Wallarah), produced at 460°C. in air	17·9	21·6	14·3	..	..
2. As (1) but produced at 500°C. in air	15·1	18·6	14·8	..	..
3. As (1) but produced at 550°C. in air	13·2	16·3	15·9	..	..
4. As (1) but produced at 600°C. in air	11·4	14·2	16·8	..	..
5. From brown coal (Yallourn), produced at 500°C. in air	22·2	25·3	5·8	..	..
6. From coking coal (Young Wallsend), produced at 500°C. in air	14·2	17·9	17·1	..	..
Static-bed Chars:					
1. From coking coal (Liddel), produced at 400°C.	19·9	22·5	9·9	..	..
2. As (1) but produced at 550°C.	7·9	9·3	11·9	..	..
3. From noncoking coal (Wallarah), produced at 500°C.	10·7	12·8	14·7	..	..
4. From coking coal (Borehole), produced at 800°C.	2·3	2·9	14·0	..	..
5. As (4) but produced at 900°C.	1·6	2·0	16·6	..	..
6. From noncoking coal (Wallarah), produced at 900°C	1·1	1·4	19·1	..	..
Noncoking Coals:					
1. Weakly caking, bituminous coal (Wallarah)	28·6	33·8	12·4	..	..
2. Brown coal (Yallourn)	45·5	54·0	3·5	..	..

were of about the same volatile content (31 per cent on air-dried basis) but of different Gieseler fluidities (16, 210, and 5,000 dial div./min.). For comparison, experiments were also carried out with other high-volatile and medium-volatile coals (V. M., 34-35 and 22-29 per cent respectively).

In respect of their volatile contents the carbonaceous inert (noncoking) additives used in the blends can be divided into three groups as follows:

(*a*) H. T. static-bed chars and coke fines prepared at 800°-900°C. with a volatile content of 1·1-2·3 per cent;

(*b*) L. T. fluidized-bed and static-bed chars produced at temperatures between 400° and 600°C. with a volatile content of 7·9-22·2 per cent;

(*c*) Noncoking coals, with a volatile content of 28·6-45·5 per cent.

OUTLINE OF TESTS

The coals were crushed to 90 per cent ($-\frac{1}{8}$ in.) and blended with coarse ($-\frac{1}{16}$ in.) or fine (−30 or −72 B.S. mesh) additives. Each charge, weighing about 190 lb., was carbonized in an 18 in. diam. Cylindrical retort heated to 900°C. in a gas-fired muffle furnace. The test usually extended over about 12 hr and was considered complete when the temperature at the centre of the charge had reached that of the wall. After it had cooled, the retort was opened and measurements made of the size grading, density, and mechanical strength of the coke according to British Standard procedures.

DISCUSSION OF RESULTS

Correlation analyses[27] of size and strength indices of coke had shown that these fall into two groups, namely (*a*) the 3 in., 2 in., and $1\frac{1}{2}$ in. shatter indices, and (*b*) the $\frac{1}{2}$ in. shatter index, the 1 in. stability factor, and the $\frac{1}{4}$ in. hardness factor, between which there are no significant relationships although close relationships exist between members of the same group. This suggests that two inherent properties of coke—macro-strength and micro-strength are involved.

In the analysis of the effect of blend variables on coke strength, $1\frac{1}{2}$ in. shatter index and $\frac{1}{4}$ in. abrasion hardness factor were taken to represent Group (*a*) and Group (*b*) respectively. To simplify the comparison of results, values obtained with the different blends were assessed on the basis of changes in strength indices compared with those of coke from the basic coal. Measured values for cokes (from basic coals) are summarized in Table 2.

To eliminate the effect of minor variations in heating conditions, measurements of coke strength were converted to the common basis of a heat-penetration rate of 0·70 in./hr, using previously established relationships between coke properties and carbonizing rates[29].

TABLE 2—PROPERTIES OF 900°C. COKES FROM BASIC COALS

	COAL		COKE PROPERTIES		
	Type	Seam	Apparent sp. gr. (60/60°F.)	1½ in. Shatter index	¼ in. abrasion hardness
1.	High-volatile, low-fluidity	Young Wallsend, St.B., (weathered)	0·90	78	76
2.	High-volatile, medium-fluidity	Yougn Wallsend, St.B., (fresh)	0·90	81	76
3.	High-volatile, high-fluidity	Fiery	0·97	80	76
4.	High-volatile, medium-fluidity	Young Wallsend, Boston	0·86	77	77
5.	High-volatile, high-fluidity	Stockton Block No. 2	0·76	60	82
6.	Medium-volatile, medium-fluidity	50-50 blend, Bulli-Wongawilli	1·01	88	69
7.	Medium-volatile, high-fluidity	Eclipse	1·00	81	76

COMPARISON OF THE EFFECTS OF DIFFERENT ADDITIVES

Type of Additive. Fig. 1 indicates the general effects of the three main types of additives (low, medium, and high V.M.) upon the shatter strength and hardness of coke from coal No. 2, a typical coal of the N.S.W. Northern Coalfield (high V.M., medium fluidity).

It is clear from Fig. 1(*a*) that the lower the volatile content of the additive, the greater the possibility of improving the shatter strength of the coke product. However, a compromise is necessary because (h.t.) chars, which give the greatest increase in shatter strength, cause a deterioration in hardness [Fig. 1(*b*)]. On the other hand, with (l. t.) chars less improvement is possible in shatter strength, but hardness can be increased. Addition of a high-volatile noncoking coal (e.g., brown coal) resulted in rapid deterioration of both shatter strength and hardness of coke as the concentration of this additive was increased.

Proportion in Blend. Fig. 1 also indicates that the improvement of shatter strength and hardness is proportional to the concentration of additive present in the blend, reaches a peak value at a certain concentration (which is 10-15 per cent for blends of the high-volatile coal of medium fluidity with −72 B. S. mesh additives), and declines when the proportion of additive is further increased.

Particle Size. Fig. 2 shows how the strength of coke from blends of coal No. 4 (high V.M., medium fluidity) with 10 per cent of l.t. char (No. 2)

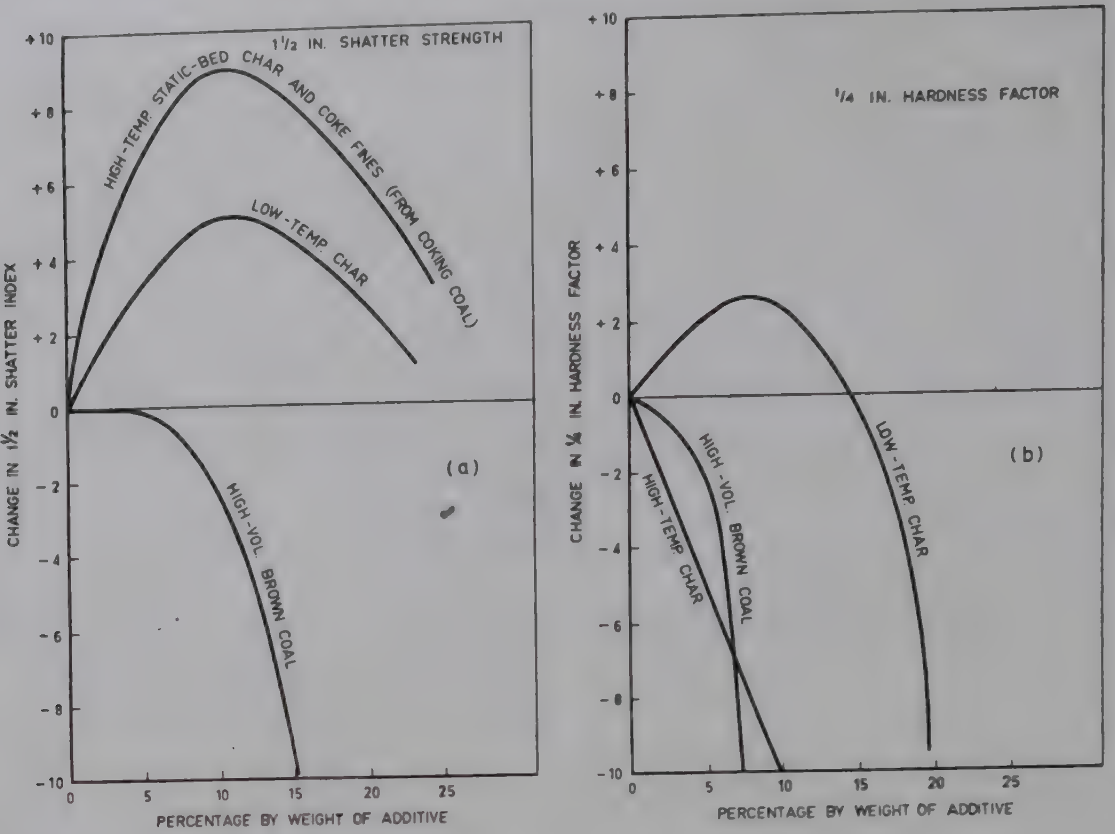

FIG. 1—GENERAL EFFECT ON STRENGTH OF COKE PRODUCT OF ADDING INERT MATERIALS (minus 72 B.S. mesh) TO A HIGH-VOLATILE COAL OF MEDIUM FLUIDITY (No. 2)

varies with the particle size of the latter. As the particle size of the additive is increased from -200 B.S. mesh to $-\frac{1}{16}$ in. the shatter strength of the coke gradually increases (rapidly at first, and then more slowly) while its hardness shows a continuous decrease. The change in charge density of blends is also shown in Fig. 2. Owing to the well known effect of charge density on coke strength[28] (an increase in the former by 1 lb./cu. ft corresponds to an increase of 1 unit in $\frac{1}{4}$ in. hardness and to a decrease of 1 unit in $1\frac{1}{2}$ in. shatter index) shatter-strength values were corrected to the same charge density basis. Comparison of the corrected and experimental curves shows that the larger the particle size of the additive the greater is the proportion of improvement in shatter strength due to reduction in charge density. The corrected curve, which can be assumed to be determined by the reduction in volatile content and, by the shape and degree of bonding of additive particles, has a maximum at minus 52 plus 72 B.S. mesh corresponding to an average particle size of 0·01 in. (250 μ) for the additive.

The fact that the hardness curve runs parallel to the charge-density curve up to a value of about 0·04 in. particle size of additive, means that the reduction in hardness with increasing particle size can be explained largely by the reduction in charge density.

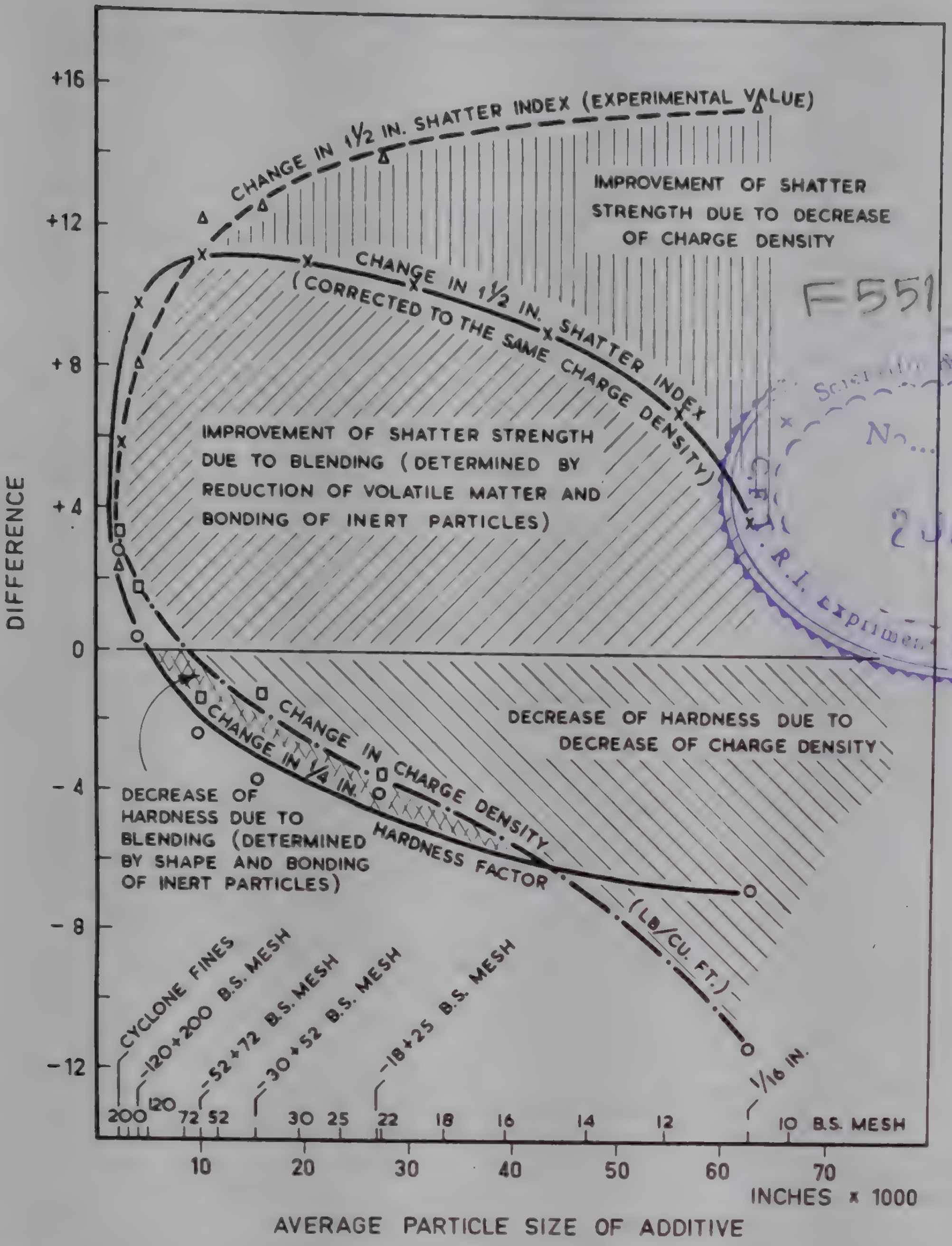

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Fig. 2—Effect of particle size of additive; the blends contained 90% high-volatile coal of medium fluidity [coal No. 4 of constant size grading, (90 per cent—1/8 in.)] and 10% low temperature fluidized-bed char No. 2 (air, 500°C.) of varying size

THE ROLE OF THE PROPERTIES OF BASIC COAL IN BLENDING

Swelling and Fluidity. Figs. 3(a) and 3(b) indicate that the greater the swelling or fluidity of the basic coal the less was the improvement in coke shatter strength, even though the addition of char gave about the same reduction in volatile content of the charge in each case. For coals of equal volatile content, swelling or fluidity can be alternatively used to predict improvements attainable by blending. In the quantitative correlations B. S. swelling number was used because it is more easily determined than fluidity.

The effect of the same factors on the hardness of coke is shown in Figs. 3(c) and 3(d). Evidently, increase in B. S. swelling number above 4½-5 or in Gieseler fluidity above 100-200 dial div./min. gives no significant improvement in coke hardness. Coals of medium swelling or fluidity gave slightly harder cokes than coals of high swelling or fluidity.

It may be concluded, therefore, that as regards possibility of improvement in both shatter strength and hardness of cokes, coals of medium swelling or fluidity are the most suitable for blending purposes.

Volatile Content. The effect of volatile content of basic coal on shatter strength and hardness of cokes from blends containing 10 per cent −72 B.S. mesh l.t. char can also be seen in Figs. 3(a), 3(b), 3(c), and 3(d). Definite experimental curves could be established only for 31-31·5 per cent and 34-35 per cent volatile-content levels, but two other points

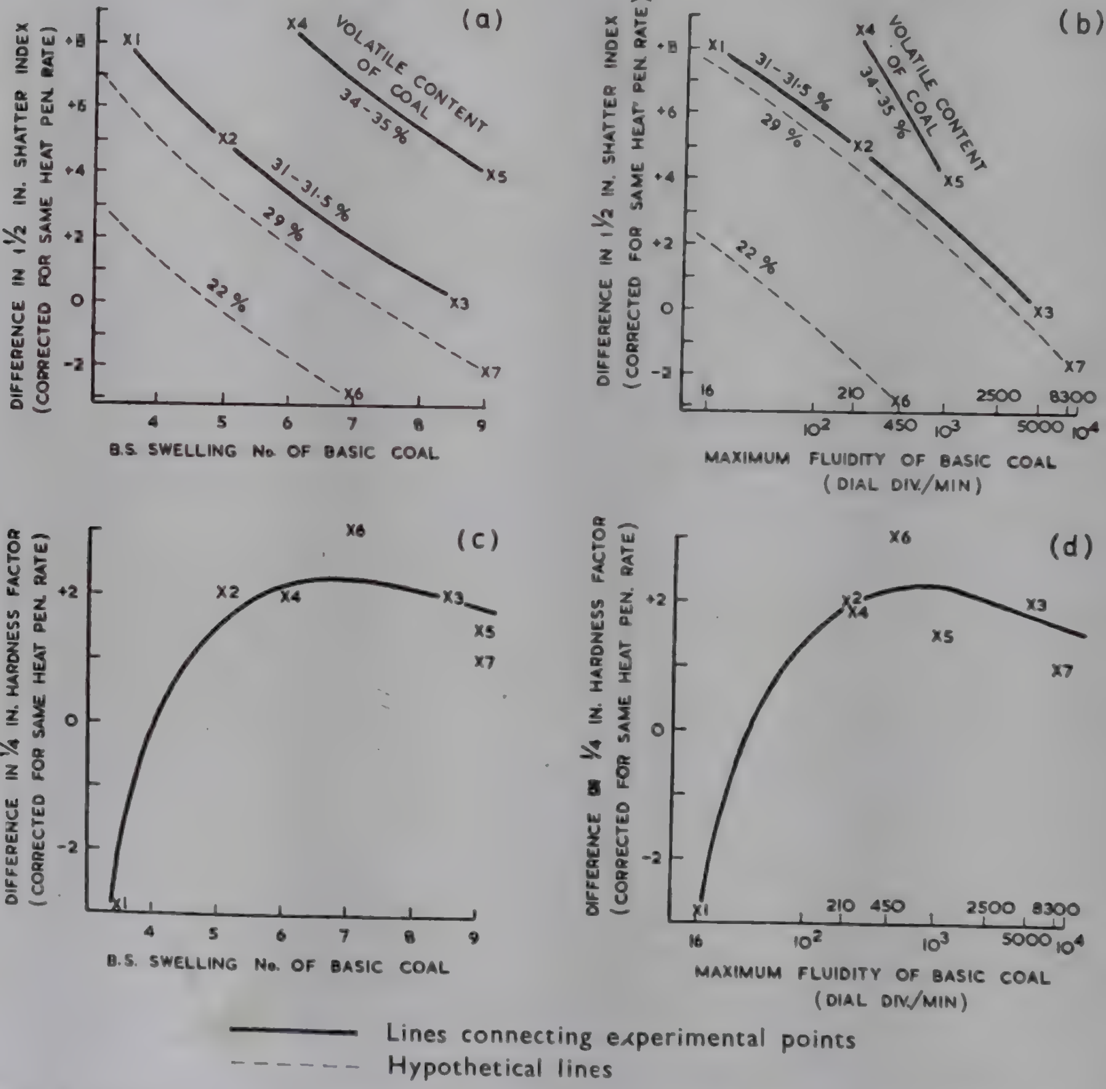

FIG. 3—EFFECT OF SWELLING NUMBER, FLUIDITY, AND VOLATILE CONTENT OF BASIC COAL ON THE STRENGTH OF COKE; ALL BLENDS CONTAINED 10% LOW-TEMPERATURE FLUIDIZED-BED CHAR NO. 2 GROUND TO −72 B.S. MESH NUMBERS AGAINST POINTS IDENTIFY COALS ACCORDING TO TABLE

(at 29 per cent and 22 per cent volatile content levels) were used to establish hypothetical lines in Figs. 3(a) and 3(b) (broken lines). These curves clearly indicate that, with a basic coal of given swelling number or fluidity, the higher its volatile content the greater is the possible improvement in the shatter strength of the coke product. Although sufficient data have so far not been accumulated to justify a quantitative assessment, the available data suggest that an increase of 1 per cent in volatile content of the basic coal—within the range studied—would correspond approximately to an increase of 0·8 unit in the possible improvement in the $1\frac{1}{2}$ in. shatter index of coke.

The increase in the hardness of the cokes was influenced only by the swelling or fluidity of the basic coal, as shown in Figs. 3(c) and 3(d) and not by its volatile content.

STATISTICAL CORRELATIONS BETWEEN PROPERTIES OF BLEND COMPONENTS AND COKE STRENGTH

Statistical analysis of the results of blend tests conducted with three coals having about the same volatile content (31 per cent on air-dried basis) but different Gieseler fluidities (16, 210, and 5000 dial div./min.) showed that the two main criteria of coke strength, namely $1\frac{1}{2}$ in. shatter index and $\frac{1}{4}$ in. hardness factor, as well as coke density and porosity, are determined by the factors discussed below:

Shatter Strength. With a view to study in more details the conclusion drawn from Fig. 1 that the lower the volatile content of the inert additive the greater the possible improvement in the $1\frac{1}{2}$ in. shatter index of the coke, the volatile content of the additives and charges was correlated with the change in shatter strength of the coke products from coal No. 2. Very highly significant correlations were established [Figs. 4 and 4A and rows 1 and 2 in Table 3], the correlation coefficients being —0·95 and —0·90 and the variance of $1\frac{1}{2}$ in. shatter index explained by the variance of volatile content 90 and 80 per cent respectively.

When the statistical analysis was broadened to include coals of a range of fluidities, both low and high, the correlation between shatter strength and volatile matter was not as good (only 57·5 per cent of the variance was explained) but it improved when a correction derived from Fig. 3 was applied to the change of volatile content, taking into consideration the swelling of the basic coal. Application of this correction increased the correlation coefficient to —0·83 and the variance explained to 68·5 per cent [Figs. 4(b) and 4(c) and rows 2 and 3 in Table 3].

Although swelling and fluidity of the basic coal are important in determining the improvements obtainable by blending, the changes in these parameters as the result of blending did not appear to be correlated with the shatter strength of the coke (rows 4 and 5 in Table 3).

TABLE 3—CORRELATION WITH SHATTER STRENGTH OF COKE

(Differences of properties from the corresponding values of basic coal and coke were used)

DEPENDENT VARIABLE (y) 1½ in. SHATTER INDEX (CORRECTIONS FOR SAME HEAT-PENETRATION RATE)* Independent variable (x)	GROUP No.†	No. OF SAMPLES	CORRELATION COEFFICIENT r	PER CENT VARIANCE EXPLAINED	LEVEL AND DEGREE OF SIGNIFICANCE‡	EQUATION OF REGRESSION LINE (y upon x)
Volatile matter content (a.d.) of additive, wt %	1 (s) (Ten per cent blends)	8	−0·95	90·0	<0·001 v.h.s.	$y= -0{\cdot}29x+10{\cdot}94$
Volatile matter content of blend, wt %	1 (s)	16	−0·90	80·6	<0·001 v.h.s.	$y= -2{\cdot}62x+7{\cdot}61$
	2 (s)	9	−0·65	41·8	0·040 f.s.	$y= -2{\cdot}03x+3{\cdot}66$
	3 (s)	24	−0·76	57·5	<0·001 v.h.s.	$y= -2{\cdot}32x+2{\cdot}41$
	4 (s)	39	−0·63	39·3	<0·001 v.h.s.	$y= -1{\cdot}77x+2{\cdot}66$
$\text{V.M.}+1/3\,(\text{B.S.S.N.}-3)\times\left(\dfrac{\%\text{ additive in blend}}{10}\right)$§	3 (s)	25	−0·83	68·5	<0·001 v.h.s.	$y= 2{\cdot}30x+3{\cdot}61$
Logarithm of maximum fluidity of blend	3 (s)	11	0·06	0·6	>0·100 n.s.	..
	4 (s)	14	0·06	0·6	>0.100 n.s.	..
B.S. swelling number of blend	3 (s)	21	−0·22	4·7	>0·100 n.s.	..
	4 (s)	37	−0·25	6·1	>0·100 n.s.	..
Volumetric shrinkage of charge, %	3 (s)§	24	−0·08	1·0	>0·100 n.s.	..

*Corrections for heat-penetration rate (in./hr): if h.p.r. >0·70, $C_1 = (\text{h.p.r.} - 0{\cdot}70)\times 27$; if h.p.r. <0·70, $C_2 = -(0{\cdot}70 - \text{h.p.r.})\times 13$.

†*Grouping of blends:*

Group 1 (s): Medium-fluidity coal with −72 B.S. mesh additives (up to 15%); Group 2 (s): Low-fluidity coal with −72 B.S. mesh additives (up to 12·5 %); Group 3 (s): Low-, medium-, and high-fluidity coals with −72 B.S. mesh additives (up to 12·5%, with the low-fluidity coal and up to 15% with the remainder); Group 4 (s): Low-, medium-, and high-fluidity coals with −1/16 in., −30 B.S. mesh, and −72 B.S. mesh additives (up to 12·5% with the low-fluidity coal and up to 15% with the remainder).

‡v.h.s. = very highly significant; f.s. = fairly significant; n.s. = not significant.

§V.M. = % of volatile content of blend (air-dried basis). B.S.S.N. = B.S. swelling number of coal

There was an absence of relationship between shatter strength and overall volumetric shrinkage of the charge, calculated from coke yield and its apparent specific gravity. This strongly suggests that blending affects not the overall shrinkage but the distribution of fissures, which is primarily dependent on the rate of volatile matter loss.

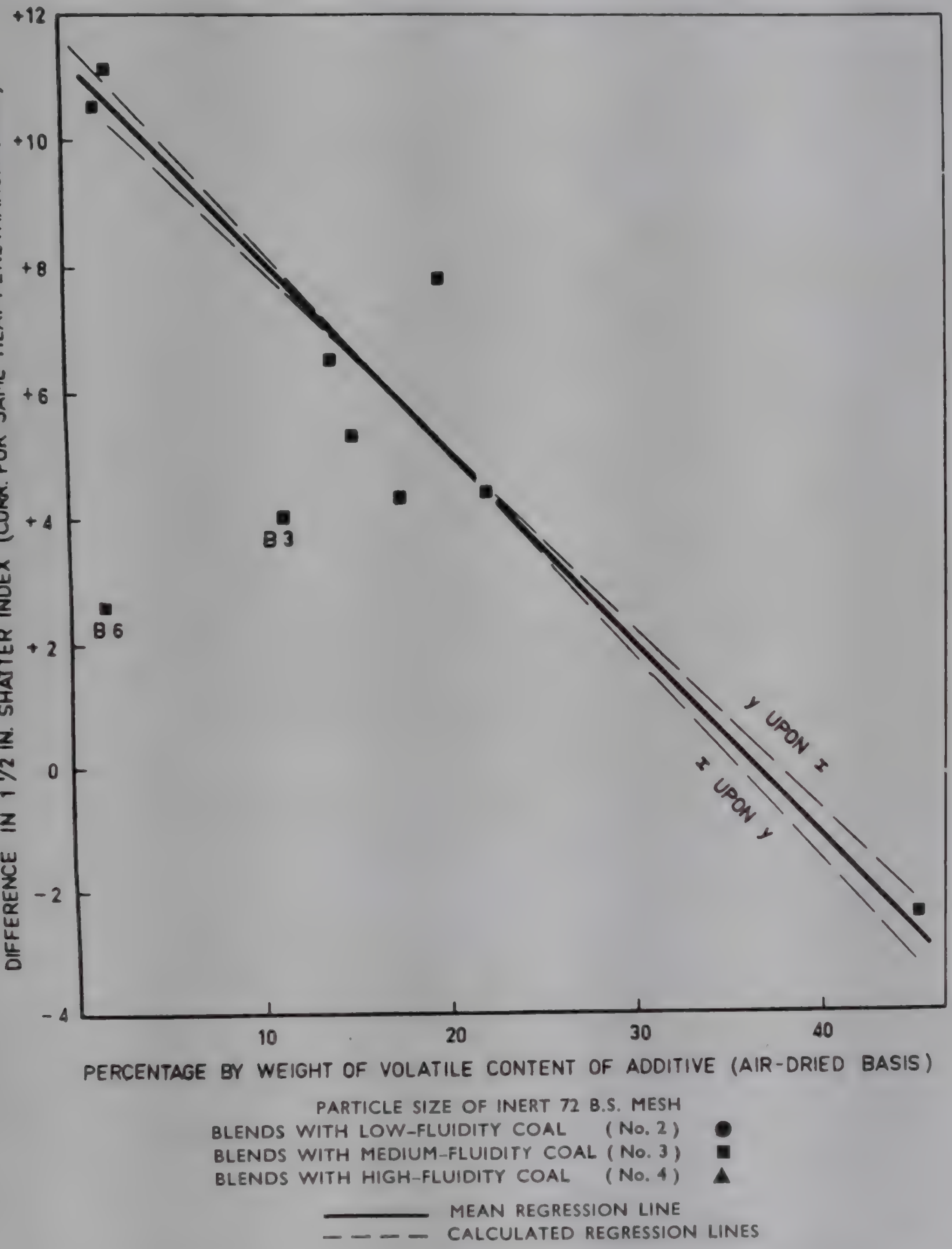

FIG. 4—RELATIONSHIP OF 1.5 IN. SHATTER STRENGTH OF COKE WITH VOLATILE-MATTER CONTENT OF ADDITIVE (minus 72. B.S. mesh) FOR 10 PER CENT BLENDS WITH MEDIUM FLUIDITY COAL

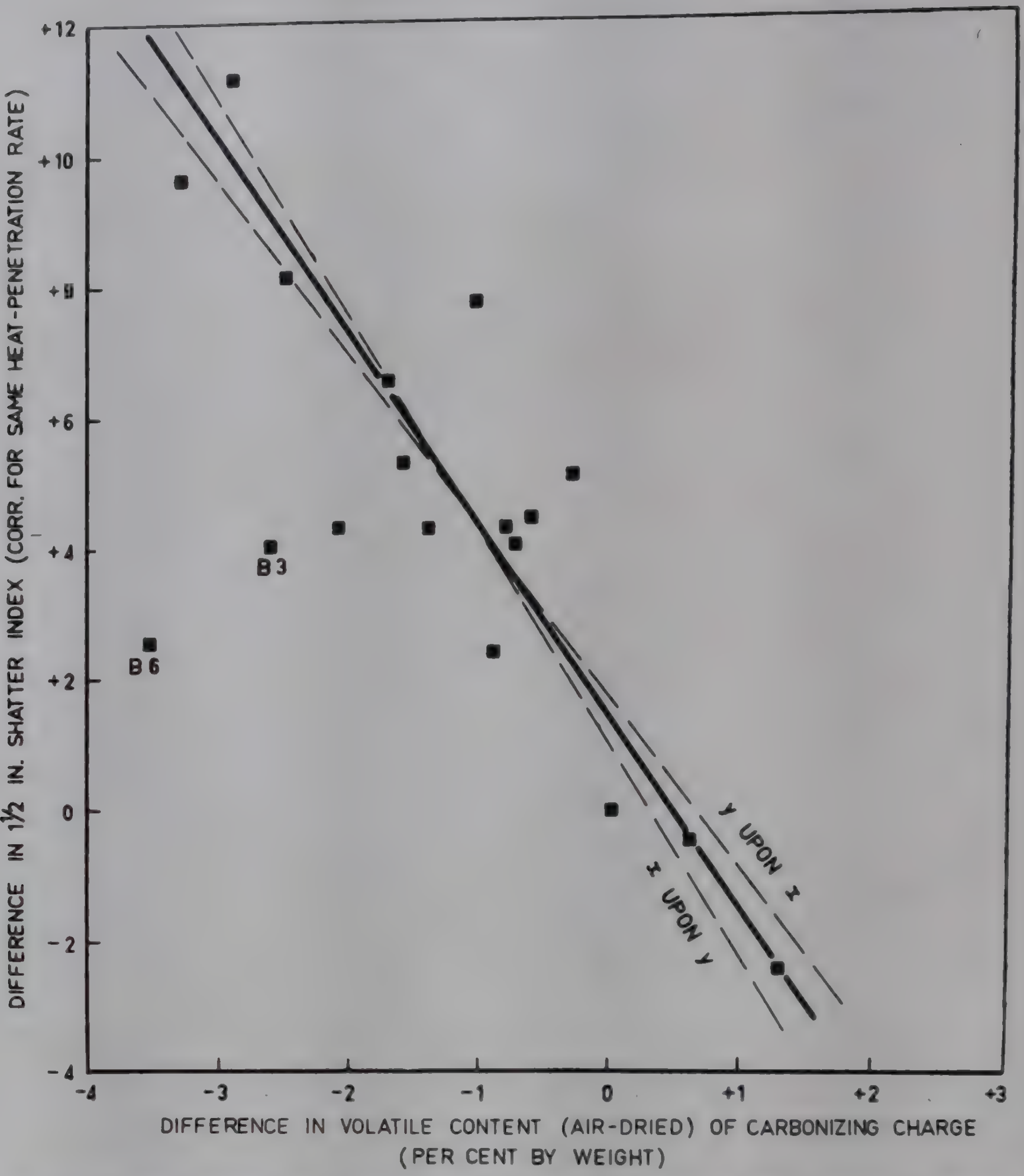

Fig. 4A—Relationship of 1.5 in. shatter strength of coke with volatile matter content of blends made from medium-fluidity coal with different concentrations of the various additives (minus 72 B.S. mesh)

Regarding the use of various types of additives, Fig. 4 shows that their effect on the shatter strength of coke is mainly determined by their volatile content, when they are prepared either from coking coal in a fluidized or a static-bed or from weakly caking coal in a fluidized bed. In Figs. 4 and 4A only the two points B3 and B6, corresponding to chars prepared from a weakly caking coal in a static-bed at 500° and 900°C. respectively, are far off the regression line. These chars did not show any degree of fusion when examined under the microscope, and they yielded much weaker cokes when used for blending than the char made from the same coal at 500°C. in a

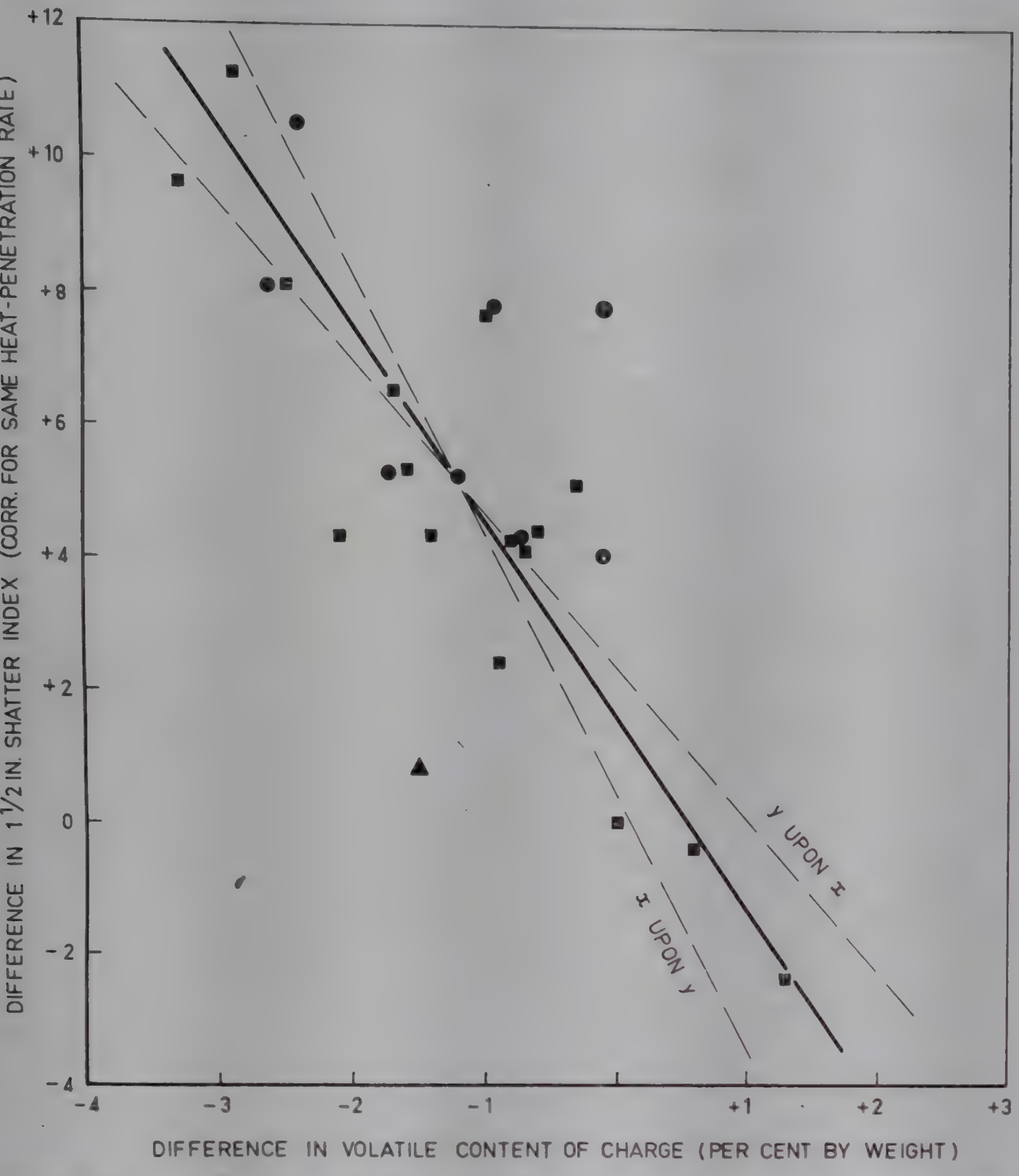

FIG. 4B—RELATIONSHIP OF 1.5 IN. SHATTER STRENGTH OF COKE WITH VOLATILE MATTER CONTENT OF BLENDS MADE FROM LOW-, MEDIUM-, AND HIGH-FLUIDITY COALS WITH VARIOUS ADDITIVES (minus 72 B.S. mesh)

fluidized bed or from coking coal at 900°C. in a static bed. It, therefore, appears that if the char is produced from weakly caking coal, the fluidized-bed technique is preferable, presumably because in this case the high rate of heating produces a certain degree of fusion and also stronger particles.

Abrasion Hardness. The close relationship which exists between the charge density of the charge and the hardness of coke product, reported by previous workers and verified in the present experiments, may be explained as follows: The bulk density determines the volume of voids in the

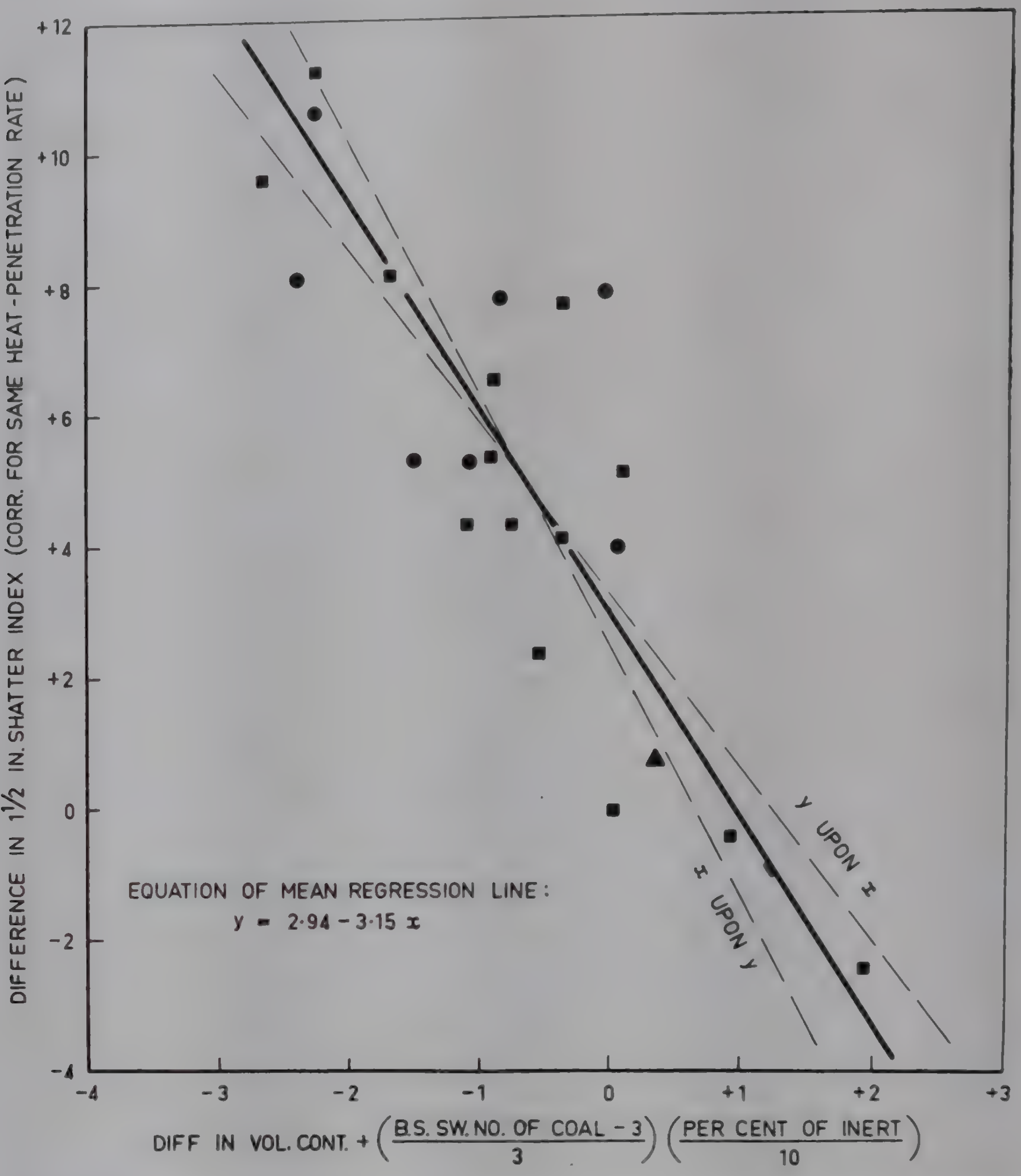

Fig. 4C—Relationship of 1.5 shatter strength of coke with relationship given in 4B modified to take into account the swelling number of the basic coal

charge into which the coal particles can swell when heated, and consequently the swelling pressure. This, in turn, decides the extent of fusion occurring in the course of carbonization, and ultimately, therefore, the degree of hardness of the coke.

To take account of the fact that when blends of coals with inert additives are carbonized, only the coal particles swell, a new parameter—the "coal charge density"—has been introduced[28] which is defined as the ratio of the weight of coal component in the blend to the volume of coal

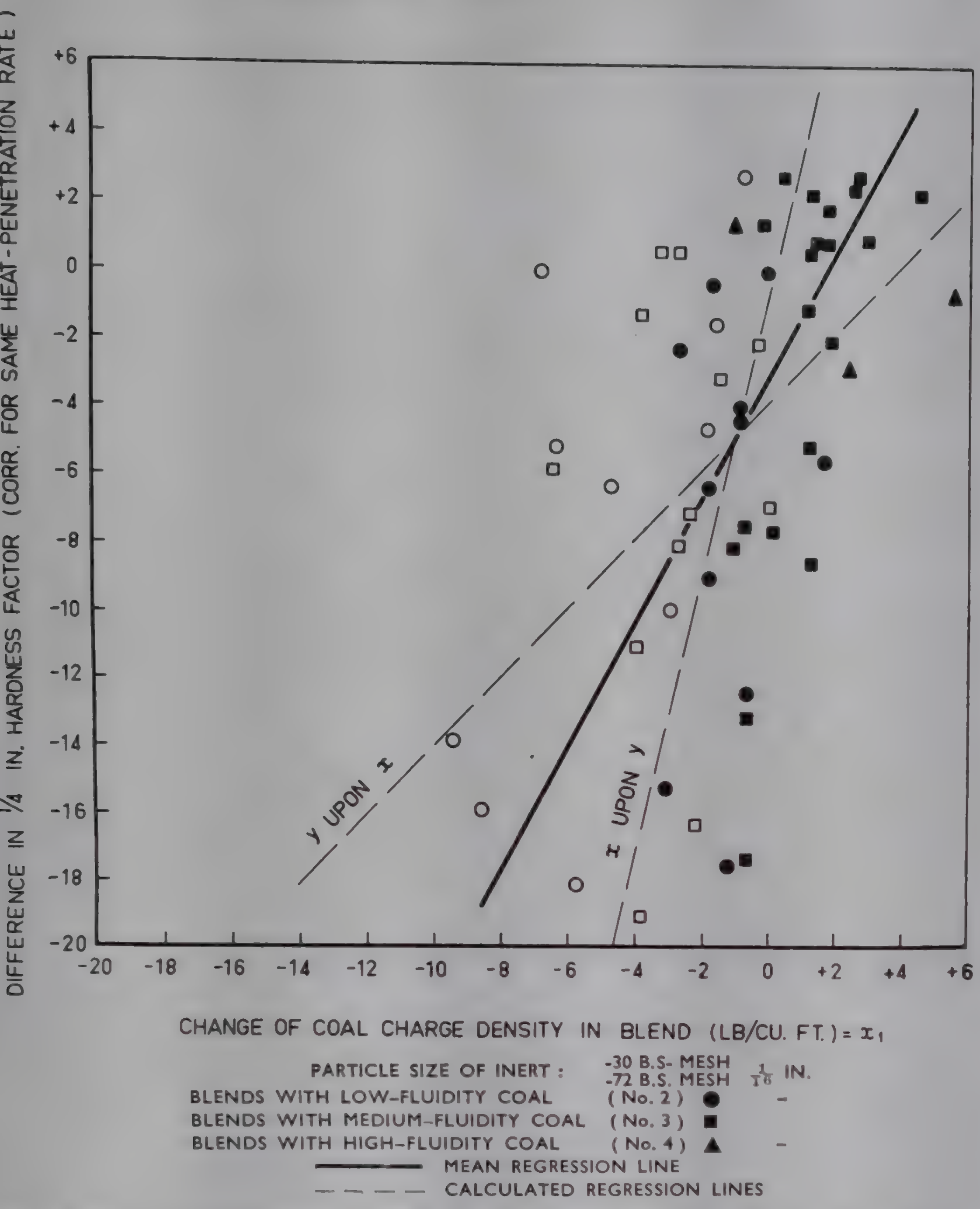

FIG. 5—RELATIONSHIP BETWEEN 0.25 IN. HARDNESS FACTOR OF COKE AND COAL CHARGE DENSITY OF VARIOUS BLENDS WITH LOW-, MEDIUM-, AND HIGH-FLUIDITY COALS

plus voids (*i.e.* on an inert-free basis)*. This has shown a highly significant relationship with the $\frac{1}{4}$ in. hardness factor of cokes from blends of various coals with different additives [Fig. 5 and row 1 of Table 4]. Thus 29 per cent of the variance of hardness can be explained.

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* The coal charge density is given by the formula:

$$CCD = \frac{\text{Weight of coal}}{Vol_{ch} - Vol_{add}} = \frac{62{\cdot}4 \times ASG \times CD \times (100 - W)}{6240 \times ASG - W \times CD}$$

where: CCD = coal charge density, Vol_{ch} = volume of charge, Vol_{add} = volume of additive, ASG = apparent sp. gr. of additive, CD = charge density of blend (lb./cu.ft), W = wt % of additive in blend.

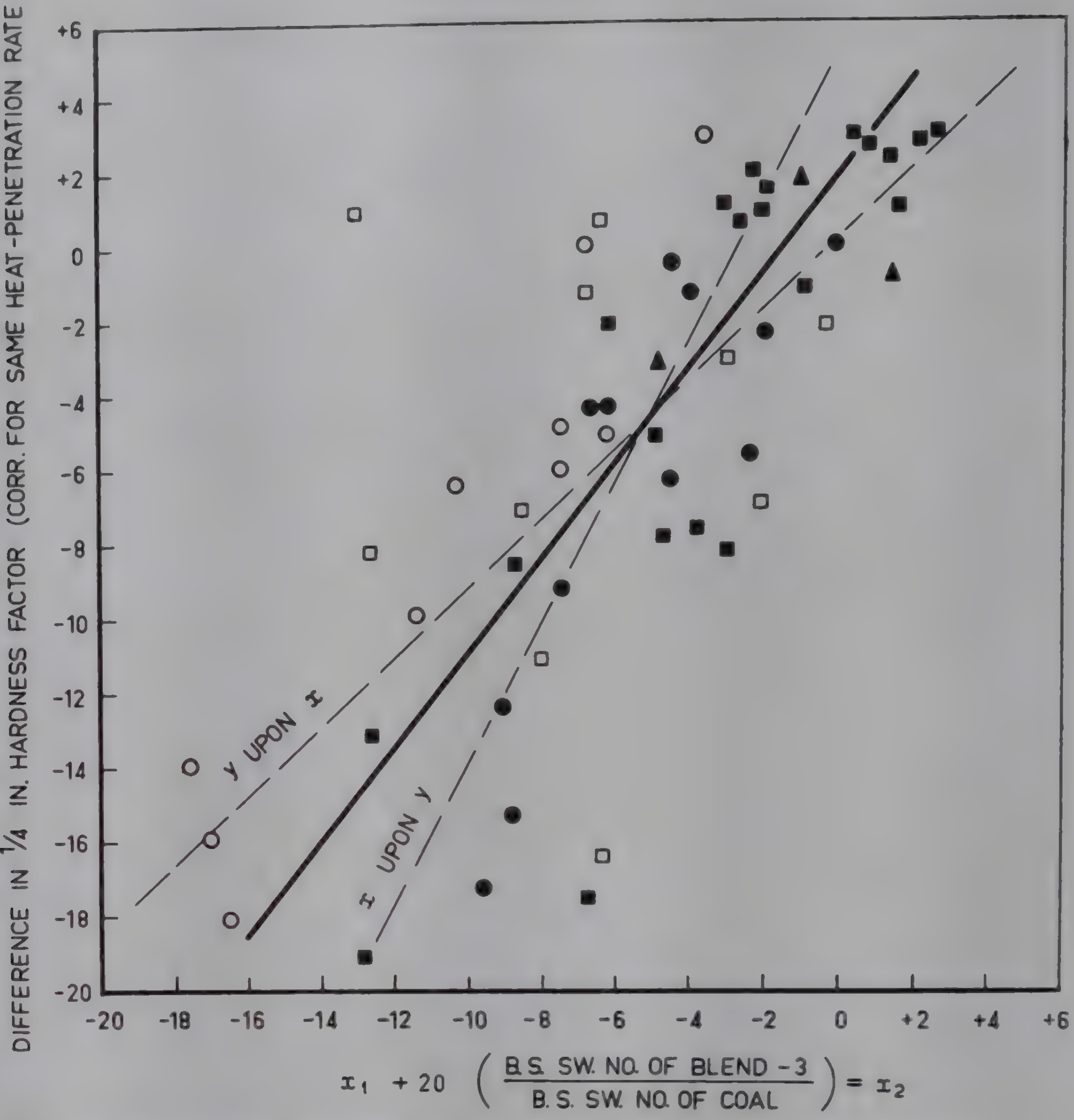


FIG. 5A—RELATIONSHIP BETWEEN 0.25 IN. HARDNESS FACTOR AND COMBINED FACTORS: COAL CHARGE DENSITY AND SWELLING NUMBER OF BLENDS

The swelling power of the original coal and of the blend are clearly among the factors which influence swelling pressure and coke hardness. In the course of the present investigation it was found that various inert additives reduce the swelling power of a given coal in almost the same way, but the extent of reduction is a function of the swelling number of the original coal[6]. A correction factor was derived taking into consideration the swelling of the basic coal and of the blend; by applying this factor in conjunction with the coal charge density factor an improvement was obtained of the correlation with hardness [Fig. 5A and row 2 in Table 4]. The variance of the $\frac{1}{4}$ in. hardness factor explained by the variance of this combined factor was 67 per cent.

A further factor which influences the abrasion hardness of coke is this "nature" of the inert additive (measured by its volatile content, except in

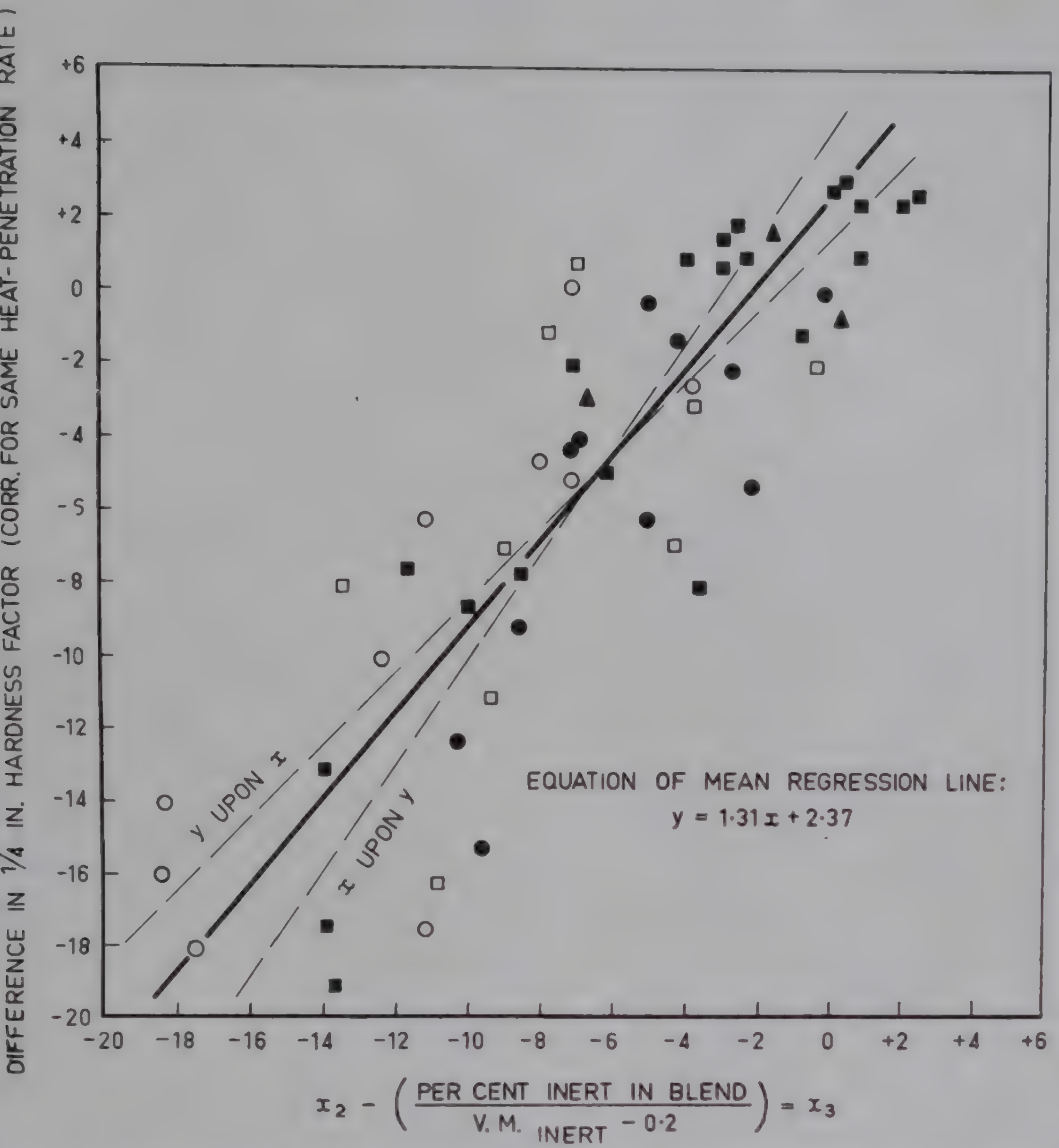


FIG. 5B—RELATIONSHIP BETWEEN 0.25 IN HARDNESS FACTOR AND COMBINED FACTORS—COAL CHARGE DENSITY, SWELLING NUMBER OF BLENDS, AND NATURE OF ADDITIVE

the case of static-bed chars prepared from weakly caking coals). It was found that from a given coal a harder coke can be produced with l.t. (500°C.) char than with h.t. (900°C.) coke fines. The reason is that in the carbonization process, particles of l.t. chars shrink to the same extent as the semicoke formed from the basic coal and therefore become "assimilated" into the coke matrix, whereas coke fines shrink to a much smaller extent and consequently in this case cavities are formed in the cell walls, resulting in a weaker coke. A correction was derived taking account of the "nature" and proportion of additive in the blend, and this when applied in conjunction with the coal charge density-swelling factor, resulted in further improvement of the correlation with coke hardness [Fig. 5B and row 3 in Table 4]. By the

TABLE 4—CORRELATIONS WITH HARDNESS OF COKE

(Differences of properties from the corresponding values of basic coal and coke were used)

DEPENDENT VARIABLE (y), ¼ IN. HARDNESS FACTOR (CORRECTION FOR SAME HEAT-PENETRATION RATE)* Independent variable (x)	GROUP No.†	No. OF SAMPLES	CORRELATION COEFFICIENT r	PER CENT VARIANCE EXPLAINED	LEVEL AND DEGREE OF SIGNIFICANCE‡	EQUATION OF REGRESSION LINE (y upon x)
Coal charge density in the blend (CCD) (lb./cu. ft) $=X_1$	3 (s)	23	0·63	39.9	<0·001 v.h.s.	$y=1{\cdot}20x-1{\cdot}24$
	3 (h)	36	0·54	29·4	<0·001 v.h.s.	$y=1{\cdot}67x-4{\cdot}63$
	4 (s)	35	0·54	29·4	<0·001 v.h.s.	$y=0{\cdot}83x-1{\cdot}58$
	4 (h)	55	0·48	23·1	<0·001 v.h.s.	$y=1{\cdot}01x-4{\cdot}05$
$X_1+20\,\dfrac{(\text{B.S. swelling number blend}-3)}{(\text{B.S. swelling number coal})}=X_2$ (correction for swelling)	3 (s)	23	0.77	59·5	<0·001 v.h.s.	$y=0{\cdot}92x+1{\cdot}02$
	3 (h)	36	0·82	67·5	<0·001 v.h.s.	$y=1{\cdot}29x+0{\cdot}78$
	4 (s)	35	0·71	50·1	<0·001 v.h.s.	$y=0{\cdot}77x+0{\cdot}55$
	4 (h)	55	0·69	47·2	<0·001 v.h.s.	$y=0{\cdot}89x-0{\cdot}31$
$X_2-\dfrac{\%\text{ inert in blend}}{\text{V.M. inert}-0{\cdot}2}=X_3$ (correction for nature of additive)	3 (s)	23	0·87	75·5	<0·001 v.h.s.	$y=0{\cdot}82x+1{\cdot}61$
	3 (h)	36	0·87	75·5	<0·001 v.h.s.	$y=1{\cdot}14x+1{\cdot}60$
	4 (s)	35	0·79	62·6	<0·001 v.h.s.	$y=0{\cdot}77x+1{\cdot}23$
	4 (h)	55	0·83	69·0	<0·001 v.h.s.	$y=0{\cdot}99x-2{\cdot}92$
$X_3-\dfrac{\%\text{ inert in blend}}{\text{V.M. inert}-0{\cdot}2}\times\left[\dfrac{20}{\text{particle size of inert (B. S. mesh)}}\right]$ (correction for particle size of additive)	3 (s)	23	0·86	74·7	<0·001 v.h.s.	$y=0{\cdot}77x+1{\cdot}79$
	3 (h)	36	0·86	74·7	<0·001 v.h.s.	$y=1{\cdot}09x+1{\cdot}84$
	4 (s)	35	0·83	68·8	<0·001 v.h.s.	$y=0{\cdot}76x+1{\cdot}66$
	4 (h)	55	0·77	59·5	<0·001 v.h.s.	$y=0{\cdot}83x+0{\cdot}94$

*Correction for heat-penetration rate (in./hr): C=−15 (h.p.r. —0.70).

†*Grouping of blends* :

Group 3 (s): Low-, medium-, and high-fluidity coals with −72 B.S. mesh additives (up to 12·5% with the low-fluidity coal and up to 15% with the remainder);

Group 4 (s): Low-, medium-, and high-fluidity coals with −1/16 in., −30 B.S. mesh, and −72 B.S. mesh additives (up to 12·5% with the low-fluidity coal and up to 15% with remainder);

Group 3 (h): Low-, medium-, and high-fluidity coals with −72 B.S. mesh additives;

Group 4 (h): Low-, medium-, and high-fluidity coals with −72 B.S. mesh, −30 B.S. mesh, and −1/16 in. additives. Cokes with ¼ in. hardness factor <60 are excluded from Groups 3 (h) and 4 (h).

‡v.h.s.=very highly significant.

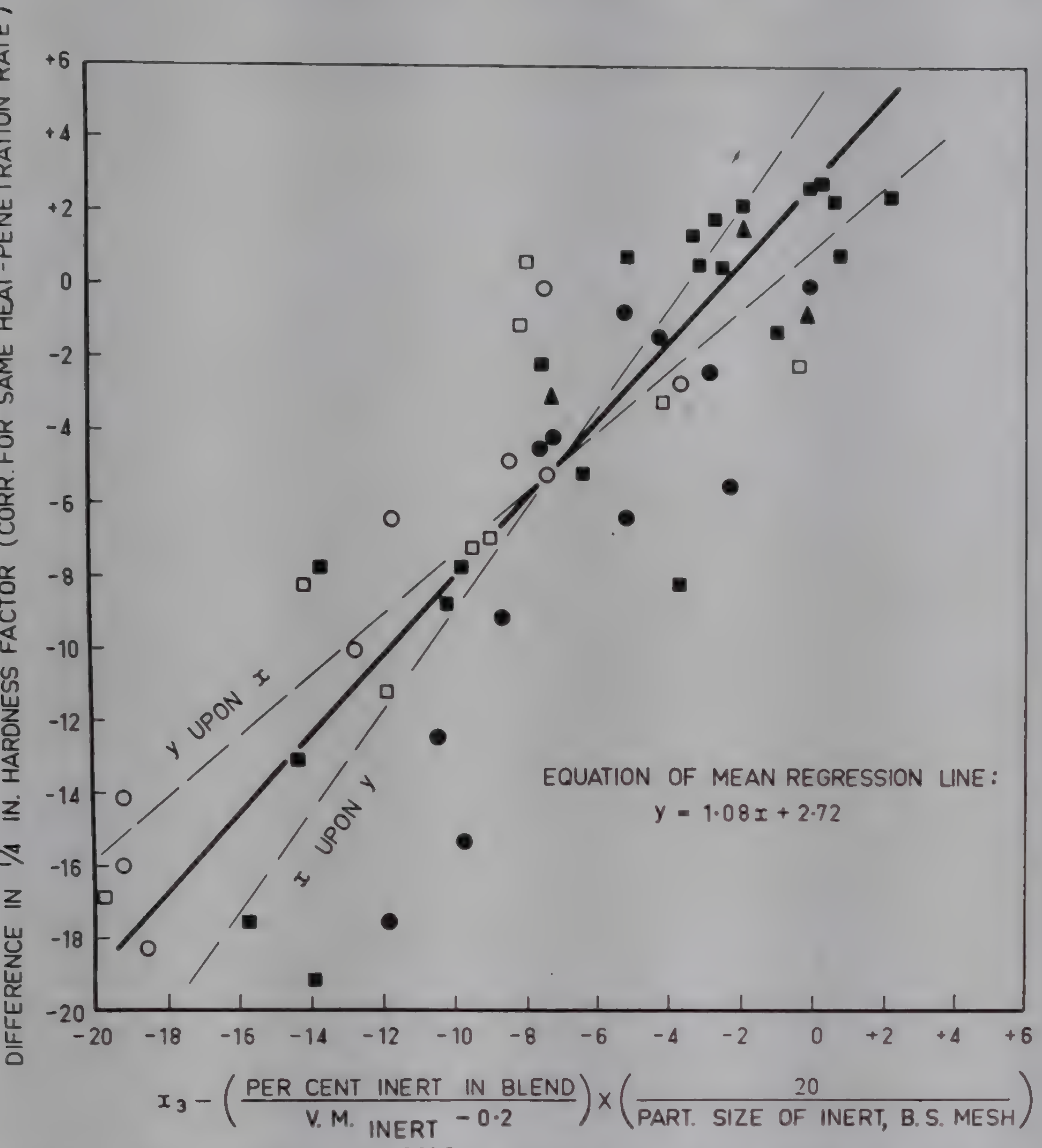


Fig. 5C—Relationship between 0.25 in. hardness factor and combined factors—coal charge density and swelling number of blends, and nature and particle size of additive

variance of this combined factor, 75 per cent of the variance of hardness can be explained.

An attempt was made to take into account also the particle size of the additive [Fig. 5C and row 4 in Table 4], but this did not improve further the already very high correlation. This was presumably because charge density had already been considered (Fig. 5) and it is also a function of particle size of additive.

Coke Density. Very close correlation was found between charge density of charge and apparent specific gravity of cokes obtained from blends of coals of equal fluidity and volatile content (Fig. 6 and row 1 in Table 5), indicating that charge density is one of the main factors determining the

TABLE 5—CORRELATION WITH APPARENT SPECIFIC GRAVITY AND POROSITY OF COKE

INDEPENDENT VARIABLE (x)	GROUP No.*	No. OF SAMPLES	CORRELATION COEFFICIENT (r)	PER CENT VARIANCE EXPLAINED	LEVEL AND DEGREE OF SIGNIFICANCE†	EQUATION OF REGRESSION LINE (y upon x)
		Dependent variable (y): Apparent sp. gr. of 900°C. coke				
Charge density (lb./cu. ft)	1 (d)	47	0·90	80·6	<0·001 v.h.s.	$y=0{\cdot}00923x+0{\cdot}40$
	2 (d)	60	0·74	54·8	<0·001 v.h.s.	$y=0{\cdot}01012x+0{\cdot}35$
		Dependent variable (y): Apparent sp. gr. of 900°C. coke $+C_1+C_2$‡				
Charge density (lb./cu. ft)	2 (d)	60	0·90	80·6	<0·001 v.h.s.	$y=0{\cdot}00992x+0{\cdot}24$
		Dependent variable: porosity of 900°C. coke, %				
Volume of voids in charge (per unit volume)§	3 (h)	38	0·83	68·5	<0·001 v.h.s.	$y=0{\cdot}44x+37{\cdot}20$
	4 (h)	55	0·93	86·5	<0·001 v.h.s.	$y=0{\cdot}49x+35{\cdot}53$
	All samples	65	0·94	88·0	<0·001 v.h.s.	$y=0{\cdot}49x+35{\cdot}53$
Porosity of semicoke (460°C.) calculated from volume of voids in charge plus volume formed by the release of volatile matter (per unit volume)**	3 (h)	38	0·89	79·4	<0·001 v.h.s.	$y=0{\cdot}42x+32{\cdot}95$
	4 (h)	55	0·93	86·5	<0·001 v.h.s.	$y=0{\cdot}53x+27{\cdot}95$
	All samples	65	0·93	86·5	<0·001 v.h.s.	$y=0{\cdot}57x+26{\cdot}15$

(Contd.)

TABLE 5—*Contd.*

INDEPENDENT VARIABLE (x)	GROUP No.*	No. OF SAMPLES	CORRELATION COEFFICIENT (*r*)	PER CENT VARIANCE EXPLAINED	LEVEL AND DEGREE OF SIGNIFICANCE†	EQUATION OF REGRESSION LINE (y upon x)
Porosity of coke calculated from volume of voids in charge plus volume formed by the release of volatile matter minus volumetric shrinkage (per unit volume)***	3 (h)	38	0·84	70·9	$<0{\cdot}001$ v.h.s.	$y=0{\cdot}62x+19{\cdot}99$
	4 (h)	55	0·89	79·4	$<0{\cdot}001$ v.h.s.	$y=0{\cdot}77x+12{\cdot}20$
	All samples	65	0·85	72·6	$<0{\cdot}001$ v.h.s.	$y=0{\cdot}66x+18{\cdot}10$

**See* Table 4. Group 1 (d): Blends of low- and medium-fluidity coals with −30 B.S. and −72 B.S. mesh additives;
Group 2 (d): Blends of all coals with −30 B.S. and −72 B.S. mesh additives.

$$^{**}V\% + 20 \times \frac{100 - V\%}{100} \times \frac{\%\ \text{coal in blend}}{100}$$

$$^{***}\text{Porosity, } \% = 100 \times \frac{\left[\dfrac{100 - (\%\ \text{coal} \times 1.4 + \%\ \text{inert} \times \text{sp. gr. inert}) \times \dfrac{\text{Coke yield } \%}{100}}{\text{True sp. gr. of coke}}\right]\left[\dfrac{100 - V\%}{100}\right] + V\% - \text{Vol. shrinkage } \%}{100 - \text{Vol. shrinkage } \%}$$

†v.h.s. = very highly significant.

‡Correction for volatile-matter content of basic coal: $C_1 = (\text{V.M. } \% - 31) \times 0{\cdot}01$. Correction for fluidity of basic coal.

$$C_2 = -(\log \text{max. fluidity} - 2{\cdot}3) \times \frac{0{\cdot}08}{1{\cdot}70}$$

$$\S\text{Volume of voids, } \% = \frac{\text{Vol. of charge} - (\text{Vol. of coal} + \text{Vol. of additive})}{\text{Vol. of charge}} \times 100 - V\%$$

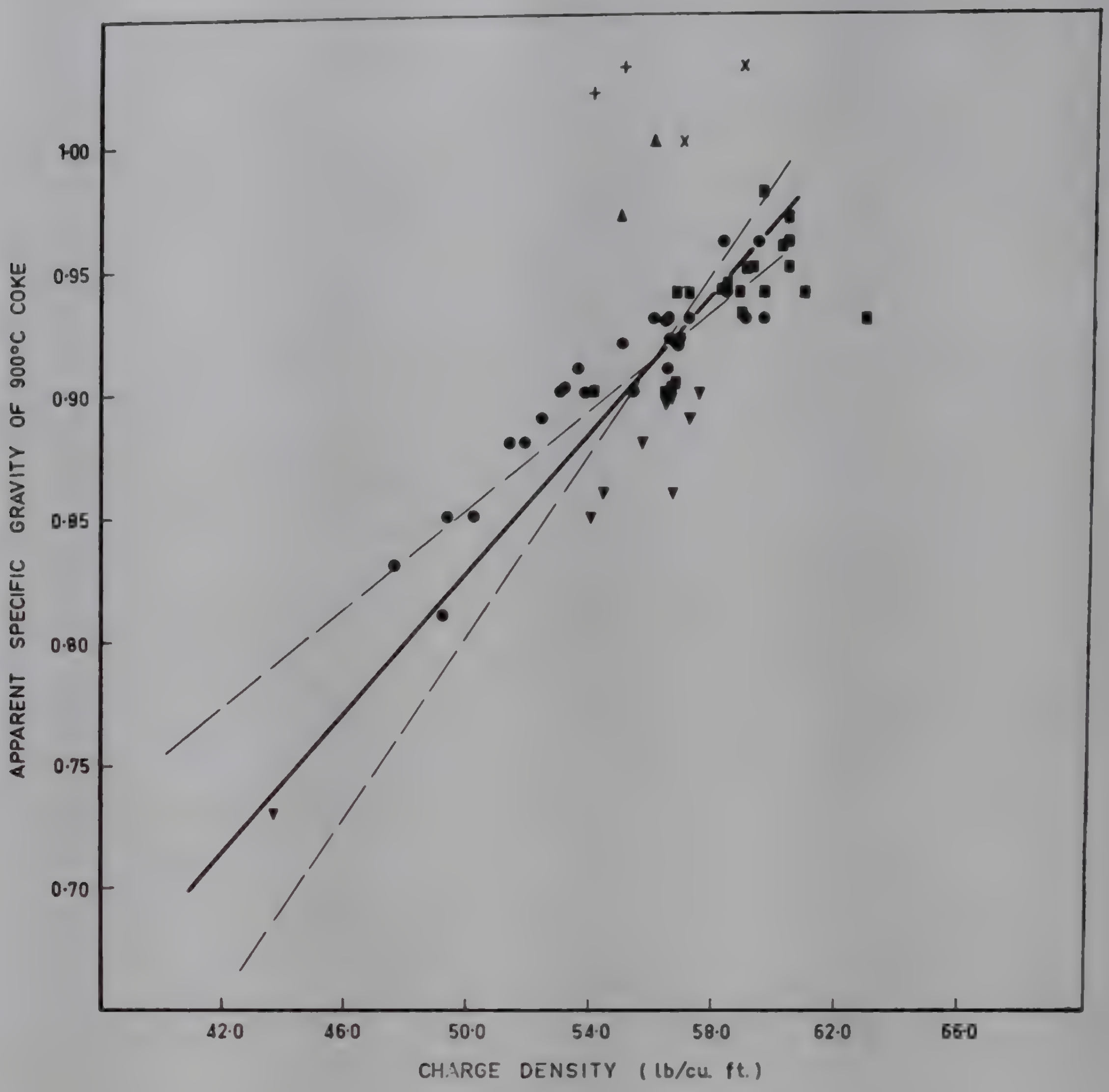


FIG. 6—RELATIONSHIP BETWEEN APPARENT SPECIFIC GRAVITY OF 900°C. COKE AND CHARGE DENSITY OF BLENDS

Symbols for Graphs 6, 6A, 6B and 6C	No. of Coal	Symbol for Blends		Vol. Cont. of Coal (a. d.)	Mix. Fluidity of Coal (dial div./min.)
		-30 and -72 B.S. mesh additive	-1/16 in. additive		
HIGH-VOL., LOW-FLUIDITY COAL	1	●	/	31–35	16
HIGH-VOL., MEDIUM-FLUIDITY COAL	2	■	□	P. C.	210
HIGH-VOL., HIGH-FLUIDITY COAL	3	▲			5000
HIGH-VOL., MEDIUM-FLUIDITY COAL	4	▼		34–35	210
MED-VOL., HIGH-FLUIDITY COAL	6	+		22	450
MED-VOL., HIGH-FLUIDITY COAL	7	×		29	8300

—— MEAN REGRESSION LINE

– – – – CALCULATED REGRESSION LINES

density of cokes. However, when cokes produced from coals of widely different volatile content and fluidity are taken into account, it becomes apparent (scattered points in Fig. 6) that the volatile content and fluidity of the basic coal also influence the density of coke. Increasing the volatile content from 30 to 40 per cent, for example, caused a decrease of 0·10 in coke density and increasing the fluidity from 200 to 8000 dial div /min. caused an increase of 0·08 in apparent specific gravity of coke, when all the other variables were kept constant. The variance of apparent specific gravity, explained by the variance of a combined factor including charge density, volatile content, and fluidity of the basic coal, was 80·6 per cent compared with 54·8 per cent when charge density alone was used [Fig. 6A and row 2 in Table 5].

When blends were carbonized, the apparent specific gravity of the coke products was usually higher than that of the coke produced from the

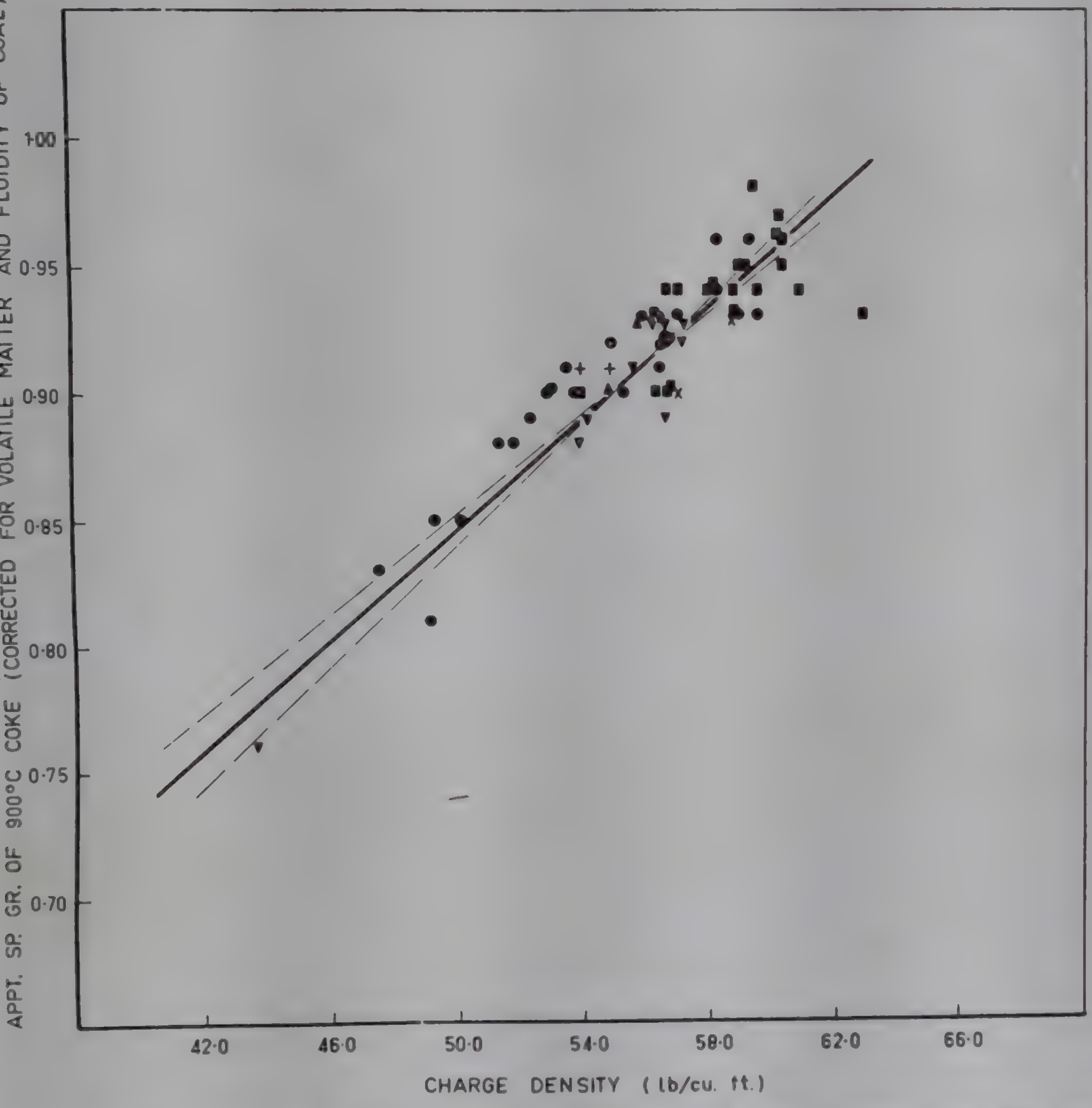


Fig. 6A—Correlation of apparent specific gravity of 900°C. coke (corrected fo volatile content and fluidity) with charge density of blends

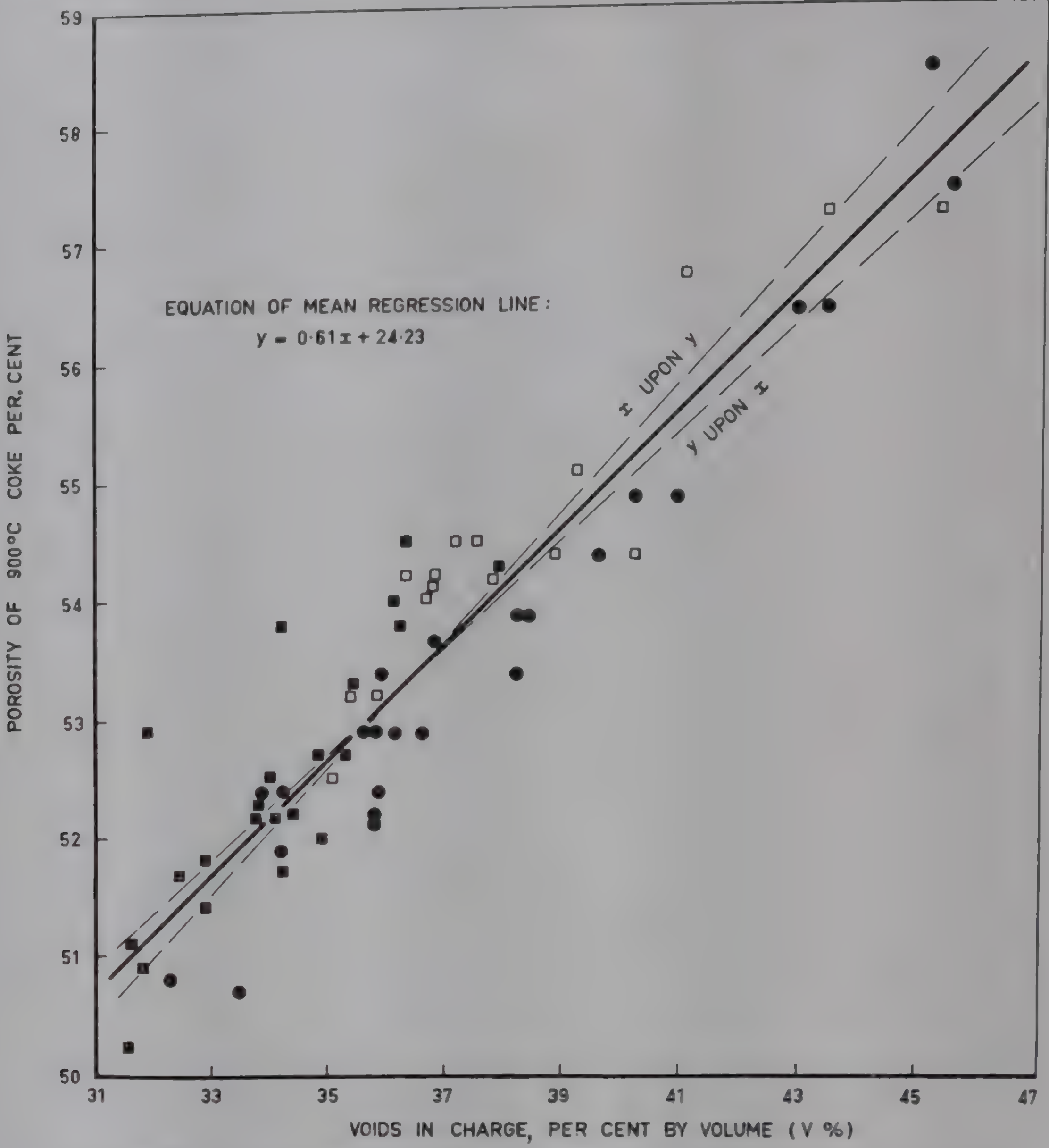


FIG. 6B—RELATIONSHIP BETWEEN POROSITY OF 900°C. COKE AND VOID VOLUME IN CHARGE

basic coal. For those cokes where both shatter strength and hardness were improved, the increase of apparent specific gravity was about 0·03.

Porosity. When the void volume of charge*, *i.e.* the free space between particles, was calculated for each of the blends and plotted against the porosity† of the corresponding 900°C. coke an extremely high correlation

---

* The percentage volume of voids was calculated from the following formula:

$$\left[1-\frac{\text{CD}}{62{\cdot}4}\left(\frac{\text{Wt. \% coal in blend}}{1{\cdot}4}+\frac{\text{Wt. \% additive in blend}}{\text{Sp. gr. of additive}}\right)\right]\times 100$$

where: CD=charge density

† The porosity of the coke (volume per cent) was calculated from the following formula:

$$P=\frac{\text{True sp. gr.}-\text{Apparent sp. gr.}}{\text{True sp. gr.}}\times 100$$

was found [Fig. 5B and row 3 in Table 5] and 88 per cent of the variance could be explained. Evidently, therefore, the void volume of the charge makes a substantial contribution to the volume of pores in the coke. Moreover, the loss of volatile matter during carbonization also contributes to the formation of pores. When the pore volume in the semicokes, which is calculated as volume of voids plus volumetric change due to loss of volatile matter up to 460°C. (the temperature of solidification), was plotted against the porosity of the final 900°C. cokes, not only was a good correlation established but also the numerical values of the porosities were close [Fig. 5C and row 4 in Table 5]. This suggests that the porosity of cokes is virtually

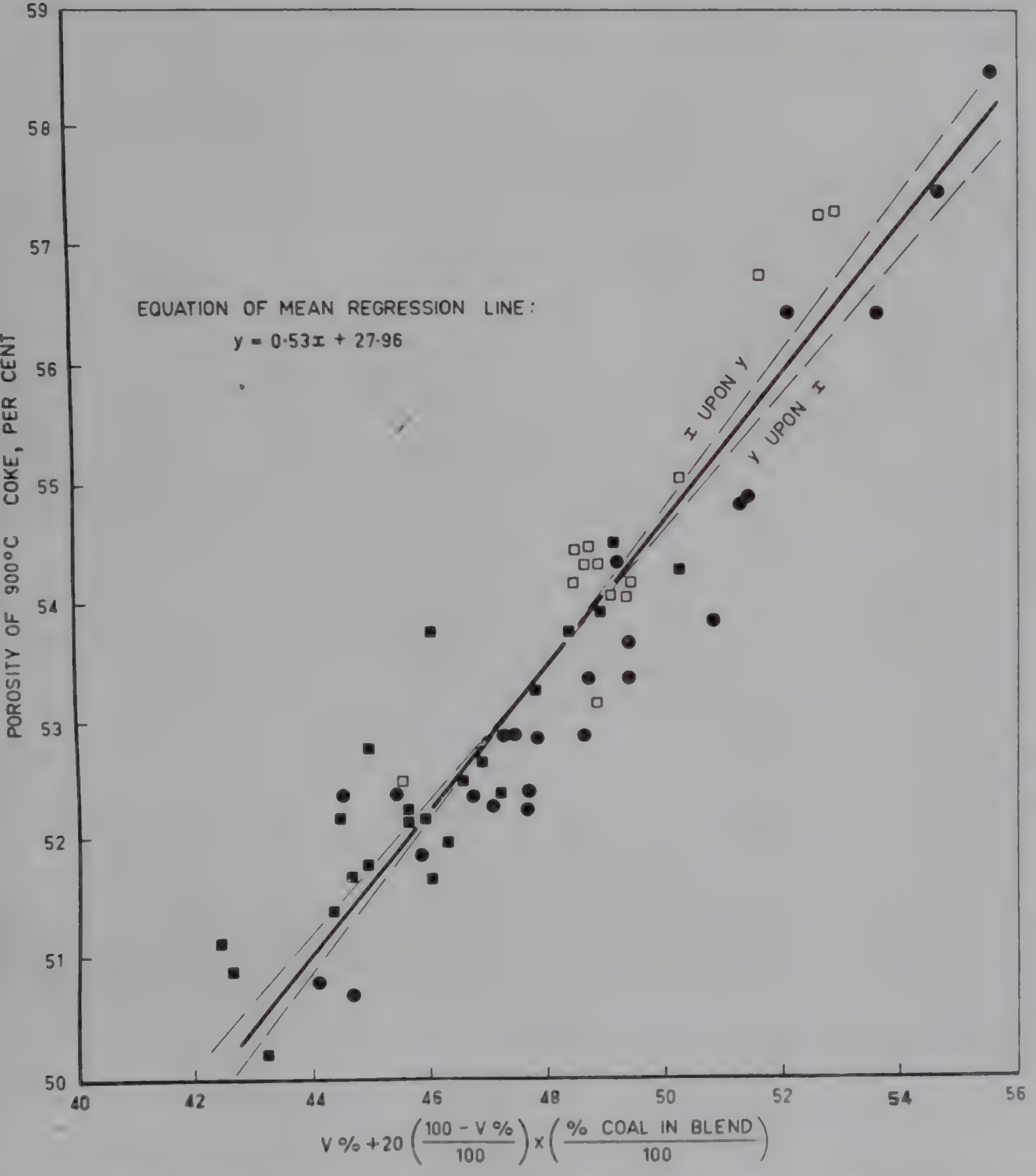


FIG. 6C—RELATIONSHIP BETWEEN POROSITY OF 900°C. COKE AND THAT OF 460°C. SEMICOKE, CALCULATED FROM VOID VOLUME OF CHARGE AND VOLUME FORMED BY LOSS OF VOLATILE MATTER

decided in the semicoke stage and that further decomposition and loss of volatile matter manifests itself in shrinkage of the coke as a whole, *i.e.* the pores shrink in a similar way to the solid semicoke. The difference in porosity between the 900°C. coke and the 460°C. semicoke from the reference coal was only 5 per cent.

Finally, the pore volume of the 900°C. cokes was calculated indirectly from the equation:

$$V_{\mathrm{p}}=V_{\mathrm{v}}+V_{\mathrm{vm}}-V_{\mathrm{s}}$$

where V_{v}=volume of voids in charge, V_{vm}=volume of space formed by loss of volatile matter, and V_{s}=volumetric shrinkage of coked mass (all related to unit volume of charge).

Very high correlation was established between the calculated and experimental data (row 5 in Table 5), which confirmed that the assumptions and measurements used in these calculations were reasonably accurate. Blending of carbonaceous inerts with coals reduces the volatile content of the carbonizing charge and increases the charge density (*i.e.* decreases the void volume in the charge). Therefore, for cokes in which the shatter strength and the hardness have both been improved by blending, a slight reduction of porosity is to be expected.

CONCLUSIONS

Analysis of the results of more than a hundred technical-scale experiments on blends of high-volatile and medium-volatile coking coals with various types of carbonaceous inert materials has led to the following conclusions concerning the factors responsible for the strength and other physical properties of coke.

Shatter Strength. Improvement in shatter strength is, within certain limits, proportional to the decrease in volatile content of the charge produced by the addition of inert material. For example, with coals of low and medium fluidity, addition of 7 per cent of finely ground (−72 B.S. mesh) l.t. char (V.M., 15 per cent) or 3 per cent of h.t. char or coke fines (V.M., 2 per cent) would decrease the volatile content of the charge by 1 per cent, which in turn would cause an increase of 3 units in the 1½ in. shatter index of the coke. Most of the variation in shatter strength can be explained in terms of volatile-matter changes.

The extent of the change in shatter strength depends on the swelling (fluidity) and volatile content of the basic coal: low-fluidity coals give the greatest change and high-fluidity coals the least, for the same amount of inert additive. The lower the volatile content of the basic coal the less improvement can be expected in the shatter strength of coke product.

Preparation of the inert additive from coking coal can be carried out either in fluidized bed or in static bed, but when non-caking or very weakly

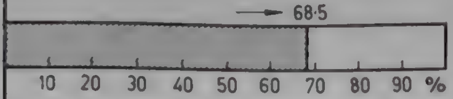
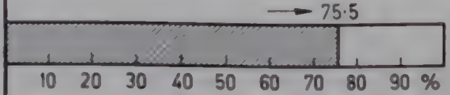
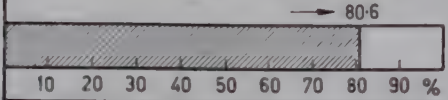
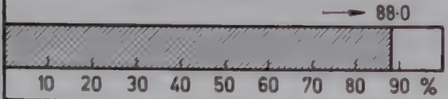
COKE PROPERTY AND % VARIANCE WHICH CAN BE EXPLAINED	BLEND VARIABLES	
SHATTER STRENGTH  	VOLATILE CONTENT OF BLEND SWELLING (FLUIDITY) OF BASIC COAL VOLATILE CONTENT OF BASIC COAL CHARGE DENSITY OF BLEND	VOLATILE CONTENT OF BASIC COAL VOLATILE CONTENT OF INERT ADDITIVE PROPORTION OF INERT ADDITIVE IN BLEND
ABRASION HARDNESS  	COAL CHARGE DENSITY SWELLING (FLUIDITY) OF BLEND NATURE (VOLATILE CONTENT) OF INERT ADDITIVE	PROPORTION OF INERT ADDITIVE IN BLEND PARTICLE SIZE OF INERT ADDITIVE IN BLEND SWELLING (FLUIDITY) OF BASIC COAL PROPORTION AND PARTICLE SIZE OF INERT ADDITIVE IN BLEND
DENSITY  	CHARGE DENSITY OF BLEND VOLATILE CONTENT OF BASIC COAL SWELLING (FLUIDITY) OF BASIC COAL	PROPORTION OF INERT ADDITIVE IN BLEND PARTICLE SIZE OF INERT ADDITIVE IN BLEND
POROSITY  	VOLUME OF VOIDS IN BLEND VOLATILE CONTENT OF BLEND	PROPORTION OF INERT ADDITIVE IN BLEND PARTICLE SIZE OF INERT ADDITIVE IN BLEND PROPORTION AND VOLATILE CONTENT OF INERT ADDITIVE VOLATILE CONTENT OF BASIC COAL

TABLE 6. SUMMARY OF EFFECTS OF BLEND VARIABLES ON COKE PROPERTIES

PARTICLE-SIZE DISTRIBUTION OF BASIC COALS (90 PER CENT $-1/8$ IN.) WAS KEPT CONSTANT IN THE EXPERIMENTS. THE INSET HISTOGRAMS GIVE THE VARIANCE OF COKE PROPERTIES WHICH CAN BE EXPLAINED BY THE VARIANCE OF BLEND VARIABLES (THESE REFER ONLY TO BLENDS OF COAL No. 2 OF HIGH VOLATILE CONTENT AND MEDIUM FLUIDITY FOR ROWS 1, 2 AND 4 AND TO BLENDS OF ALL COALS FOR ROW 3). THE MAIN VARIABLES AFFECTING A CERTAIN COKE PROPERTY ARE UNDERLINED caking coal is used as raw material, the fluidized-bed technique is preferable. The optimum particle size of additive is minus 52 plus 72 or minus 72 plus 120 B.S. mesh. Blending gives less improvement in shatter strength if the particle size of the additive is less than this.

Abrasion Hardness. The change in the $\frac{1}{4}$ in. hardness factor, for a given coal, was found to depend partly on the change in coal charge density, partly on the change in the British Standard swelling number caused by blending, and partly on the nature (volatile content) and particle size of additive. The coal charge density—a newly derived factor, is related to the inter-particle swelling pressure developed during coking. This and the fluidity of the charge determine the degree of fusion, which is the main criterion for the formation of coke.

The volatile content and particle size of additive are other important factors, because they determine the extent of assimilation of the inert particles into the coke matrix. L.t. chars give the best results, because they shrink to the same degree as the coal semicoke. Fine grinding of additives is desirable, because fine particles become better enveloped in the cell walls than coarse ones, and they also increase the coal charge density.

Coke Density and Porosity. As a general rule, an increase of 10 lb./cu.ft in the charge density causes an increase of about 0·10 in the apparent specific gravity of coke obtainable from blends of a given coal with various additives. This correlation can be extended to blends of various coals, if the volatile content and fluidity of the basic coal are taken into consideration.

Table 6 summarizes these findings and shows how the physical properties of coke are determined by the volatile matter content, particle size, and proportion of inerts used for blending, and also by the properties of the basic coal.

One practical conclusion which can be drawn from this analysis is that improvement in shatter strength of coke from a high-volatile coal can be secured without accompanying loss of abrasion hardness; indeed, the hardness may even be increased. The general conditions of blending necessary to achieve this improvement are:

(1) The inert material should have a volatile matter content similar to that of the semicoke from the coal about its solidification point (*i.e.* approx. 15 per cent), and should be reasonably fused.

(2) Fine grinding of the inert particles is preferred, either to minus 52 plus 72 B.S. mesh or to minus 72 plus 120 B.S. mesh, as it facilitates efficient incorporation of the particles in the cell walls of the coke.

(3) The basic coal should be medium swelling (B.S. swelling number 5-6) and high-volatile (air-dried V.M. $>$ 30 per cent).

The results of the statistical analysis of blend data at 31 per cent volatile content level enable not only rules for the preparation of oven charges to be formulated, but also predictions of the coking behaviour of charges from simple basic information on the charge components such as, volatile matter, B.S. swelling number, charge density, and nature of inert.

ACKNOWLEDGEMENT

The work formed part of the research programme of the Division of Coal Research, C.S.I.R.O., and the author's thanks are due to H. R. Brown, Chief of the Division, for help and guidance; as well as to many other colleagues including, in particular, Dr P. L. Waters, Dr K. McG. Bowling, Dr G. H. Taylor, W. T. Cooper, and J. Grieve for their generous assistance.

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Development of Hykol Active Carbons from Kolsit

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S. H. ZAHEER

Regional Research Laboratory
Hyderabad

Active carbon prepared from the semicoke obtained in an internally heated low temperature carbonization plant has proved to be a good decolourizing agent. Work done with various types of reactors is reported and based on these data a semi-commercial plant to produce half-a-ton of active carbon per day is being set up.

Almost every carbonizable material has been used for the production of active carbon; but recently mineral coal is coming into prominence as a raw material for active carbon[1–6]. Four different non-caking high-ash coals from Singareni, Tandur, Upper Kajora and Jambad were tried in this Laboratory and Singareni coal was found to be more suitable for the preparation of active carbon[7–8].

Carbonization at a temperature of 650°C. using the method of internal heating by recirculation of combustion gases is effective in producing the necessary surface and capillary structure in the semicoke rendering it suitable for bleaching of vegetable oils. It is further activated by steam to get decolourizing carbons suitable for use in refining and purification of sugar, glycerine and pharmaceuticals and decolourization of dark-coloured vegetable oils. The active carbon for bleaching of vegetable oils is being manufactured in this Laboratory on behalf of the National Research Development Corporation of India and is marketed by Messrs Voltas Ltd, under the trade name Hykol 'O'.

Hykol 'X' and Hykol 'BC', other two grades of decolourizing carbons manufactured in the Laboratory by steam activation, are also being supplied to the industry. However, the commercial production of these two grades is still in initial stage of development.

This paper deals with the pilot plant experiments carried out in different reactors with a view to collect data for the designing of a suitable unit.

STEAM ACTIVATION OF KOLSIT

Activation of kolsit (the semicoke obtained by low temperature carbonization of Singareni coal) was carried out in the Laboratory in a fireclay crucible in an electric furnace under the following conditions for obtaining good products. Temperature 850-900°C.; Feed size, 6-12 mm.; Degree of oxidation, 50-60 per cent of fixed carbon.

ACTIVATION IN INTERNALLY HEATED BATCH ROTARY KILN

A batch oil-fired rotary kiln of 30 cm. internal diam. and 90 cm. length lined with refractory material was used as a reactor. Steam was passed into the material from the end opposite to the burner. The material thus produced was found to lose its activity on keeping and further, during grinding using mechanical grinding equipment. The activity of the samples obtained in mechanical grinding equipment was always less than that given by the sample ground in pestle and mortar by hand. Direct heating of the material during steam activation had to be abandoned in spite of its advantages of fuel economy and cheaper material of construction. It is believed that activation in drastic conditions, as in the case of direct heating, weakens the pore structure of carbon leading to slow blockage of the pores. This appears to be accelerated by subjecting the material to grinding.

ACTIVATION IN EXTERNALLY HEATED VERTICAL REACTORS

A cast iron pipe of 15 cm. internal diam. placed vertically and heated externally in an oil-fired furnace was next used as a reactor. Kolsit was fed from the top of the reactor while steam was introduced at the bottom. The product was withdrawn from the bottom at desired intervals. The quantity discharged each time was regulated to give the required residence time for the material. The product obtained from this reactor had good activity and did not suffer from the drawback of deterioration in activity. However, the life of the reactor was found to be very short.

Next 18 8 quality stainless steel pipe of 20 cm. diam. was used in the pilot plant. The steam activation pilot plant (Fig. 1) consists of the 20-cm. diam. tubular reactor with a feed hopper and a valve on the top and a screw discharge unit at the bottom. The reactor has three zones for preheating, heating and cooling and is heated to the required temperature externally by an oil-fired furnace. Two steam nozzles are placed inside the reactor below the hot zone. When the hot zone has attained a temperature of 850-900°, superheated steam heated to 350-400°C. is admitted into the reactor at the required rate. After a given interval of time, a specified

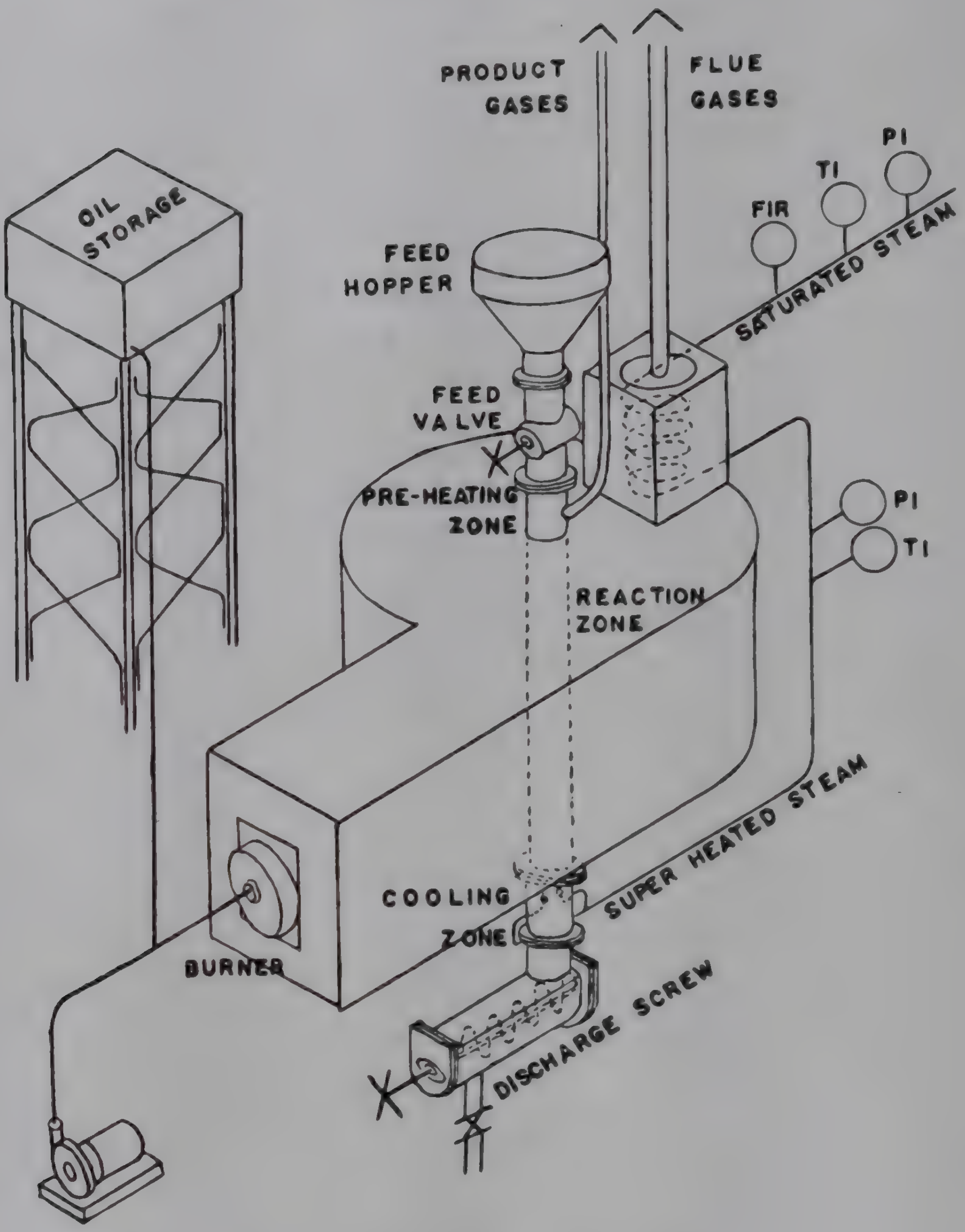
PRODUCT GASES
FLUE GASES
PI
TI
FIR
SATURATED STEAM
OIL STORAGE
FEED HOPPER
FEED VALVE
PRE-HEATING ZONE
PI
TI
REACTION ZONE
SUPER HEATED STEAM
COOLING ZONE
BURNER
DISCHARGE SCREW

FIG. 1—STEAM-ACTIVATION PILOT PLANT

quantity of material is taken out from the bottom. The whole bed of coke in the reactor thus moves down after every discharge and fresh coke is fed to make up the level at the top. The operation of the pilot plant thus becomes continuous. The product is dried, ground to required fineness in a ball mill and tested for its decolourizing activity. Operating at 900°C., the life of the 18/8 quality stainless steel reactor was found to be about 3000 hr. The product obtained at this temperature and at coke to steam ratio of 1 : 6 has a molasses decolourization value of 60-70 per cent. The fuel oil consumption was found to be 8 litres/hr for an output of approximately 30 kg. of active carbon in 24 hr.

For scaling up of the plant, experiments were carried out using reactors of 10, 20 and 30 cm. diam. The performance of the 20 cm. diam. reactor was found to be most satisfactory. This indicates that for designing a higher capacity unit increasing the diameter of the reactor beyond 20 cm. is not useful and hence multiple reactors of this size will have to be used.

With 30 cm. reactor, the capacity did not increase proportionately. On the other hand, the quality of the material was adversely affected. This appears to be due to the semicoke in the central core of the reactor not being at the desired temperatures, resulting in inadequate reaction with steam. In the product withdrawn from the reactor the less active material from the central core gets mixed with the more active material from the periphery, thus lowering the overall activity of the product. It was concluded that heat transfer from the furnace to the coke inside the reactor takes place adequately to a depth of 10 cm. only, the material lying beyond being at a lower temperature reacts more slowly.

To verify this, experiments were conducted in a 30-cm. pipe having a 10-cm. pipe concentrically inside it. The coke was fed into the annular space thus reducing the distance of heat transfer to 10 cm. without appreciable change in the area of cross-section of the reactor. Performance of this reactor was found to be satisfactory both with regard to quality and quantity of the product.

Thus, for achieving higher capacities, pipes of diameters larger than 20 cm. can also be used, provided inner pipes of suitable size are chosen to give a heat-transfer distance of 10 cm.

At present, in India, 300 tonnes of active carbons, of various grades are being produced annually, while the imports in 1960 were to the tune of 460 tonnes[8]. Hykol carbons have been found to compare favourably with the imported good quality decolourizing carbons[9]. Some characteristics of Hykol carbons are compared with those of an imported carbon, Darco S-51 in Table 1.

TABLE 1—CHARACTERISTICS OF HYKOL CARBONS COMPARED WITH DARCO S-51

	CARBON %	ASH %	HCl SOLUBLE %	pH OF WATER EXTRACT	SURFACE AREA m^2/g.
Darco S-51	65-70	25-30	0·5	4·5-6·0	512*
Hykol 'X'	50-55	35-40	5·0	7·0	513*
Hykol 'BC'	60-65	25-30	5·0	7·0	145**
Hykol 'O'	65-67	23-25	5·0	7·0	24

*Determined by B.E.T. method.
**Determined by benzene adsorption method.

A project for establishing a semi-commercial plant to produce 0·5 ton Hykol 'X' per day at this Laboratory, has been sanctioned by the National Research Development Corporation of India. When this plant goes into production it is expected to help in reducing the imports, thereby saving foreign exchange to the extent of Rs 2·5 lakhs every year.

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DISCUSSION

Shri M. C. Bakshi: (1) The fineness and bulk density of the active carbon are not mentioned in the paper. They are important for industrial purposes. (2) The percentage of insolubles in acid is not given. Active carbon is used in acid, alkaline or neutral medium in industry and it should not contain anything soluble in acids. (3) Will a plant to produce 30 kg./24 hr of active carbon be economical ?

Dr M. Vahrman: I should like to draw the attention of the authors to the work done by the British Coal Utilization Research Association in the U. K. on coals of different ranks. These were carbonized at different temperatures, and subsequently steamed. By this means chars of different porosities could be obtained having molecular sieve properties. By selection of the appropriate char, removal of specific components from mixtures, industrial clarification of various types, etc. could be effected. Are the authors aware of this work ?

Dr S. K. Sircar: I would like to enquire why active carbon obtained by using rotary kiln is deteriorating in quality ?

Dr R. Kaparthi: I would like to know whether activation in fluidized bed has been tried as heat transfer in fluidized bed is high. The authors state that 20-cm. bed is more effective than 30-cm. bed. It may be that in a fluidized condition, 30-cm. bed may also be equally effective.

Dr Y. Venkatesham: First with reference to the point raised by Shri Bakshi, work on preparation of active carbons with very little acid soluble material is at present in progress. The raw material has a high ash content and so also the product. The *p*H of the active carbon is near neutral and its ash is not dissolved in the processes carried out at near neutral conditions. Regarding the economic size, the 30 kg./24 hr unit is only a pilot plant meant to produce sufficiently large quantities of samples and to collect data for designing bigger plants. The product from even this unit is able to compete successfully with imported material. We are proposing to instal a plant with a capacity of 1/2 ton per day.

With regard to Dr Vahrman's question our aim has been to produce active carbon from the coal available locally. We are already in the know of the work done at the BCURA laboratories.

With reference to the point raised by Dr Sircar, it may be that in the rotary kiln, due to the coke being directly exposed to drastic conditions, the macropores of the carbon collapse causing deterioration in quality. There is, however, no experimental evidence on this point.

I agree with Dr Kaparthi that in a fluidized reactor a bed diameter of 30 cm. or more can be used. However, the experiments reported here were done in fixed beds using reactors of various diameters and the reactor with 20 cm. diam. gave the best performance.

Combustion of Low Temperature Semicoke on Open Grates

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Combustion tests on semicoke (obtained from carbonization of Kothagudem coal at 650°C.) in an oven showed that semicoke can be lighted in 10-25 min. depending on the size of fuel and clearance between grate bars. Rate of combustion could be reduced by more than 50 per cent by starting with low natural draught and slow throttling of the draught in stages, thereby prolonging the period of useful heating. Details of oven, grate area and size of semicoke used are given.

In India, the main aim of production of semicoke by low temperature carbonization (l.t.c.) of coal is to provide a reactive smokeless solid fuel which can substitute charcoal, firewood and other domestic fuels used by a great majority of population. Low temperature (l.t.) semicoke is expected to find its major use as a fuel in domestic kitchens and commercial catering establishments. In most parts of India, space-heating by bright radiant heat is not a necessity.

In order to serve its purpose as a satisfactory domestic fuel, l.t. coke should have the following essential characteristics of combustion: easy ignitability; high reactivity; steady combustibility; capacity to give sufficient radiant heat; and smokeless combustion. Of these, ignitability, reactivity and smokeless combustion of the semicoke are essentially dependent on the conditions of carbonization, particularly the temperature and time, and also the nature of coal. The remaining two characteristics are mostly controlled by the design and conditions of operation of the oven used for combustion of semicoke. Slow and steady combustion and supply of uniform heat are the main requirements of a domestic oven and these are mainly controlled by the design features of the oven.

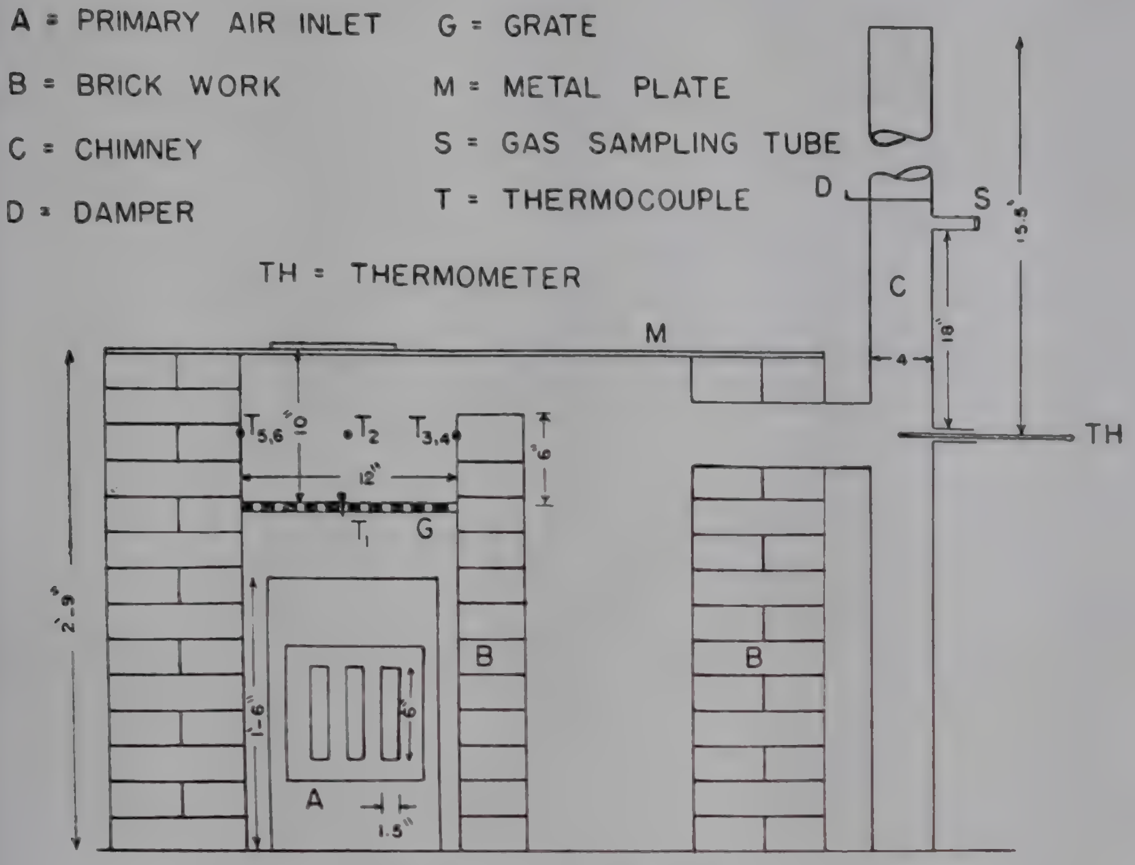
The present work was undertaken to study the combustion characteristics of semicoke produced in the Lurgi-Spuelgas l.t.c. pilot plant at this Laboratory, with a view to collect data for the design of ovens to suit different requirements. The semicoke used in the tests was obtained by carbonization of Kothagudem coal at 650°C. and had the following proximate analysis: moisture, 4·4; ash, 21·7; volatile matter, 7·7; and fixed carbon, 66·2 per cent and calorific value, 11,050 B.t.u./lb.

EXPERIMENTAL

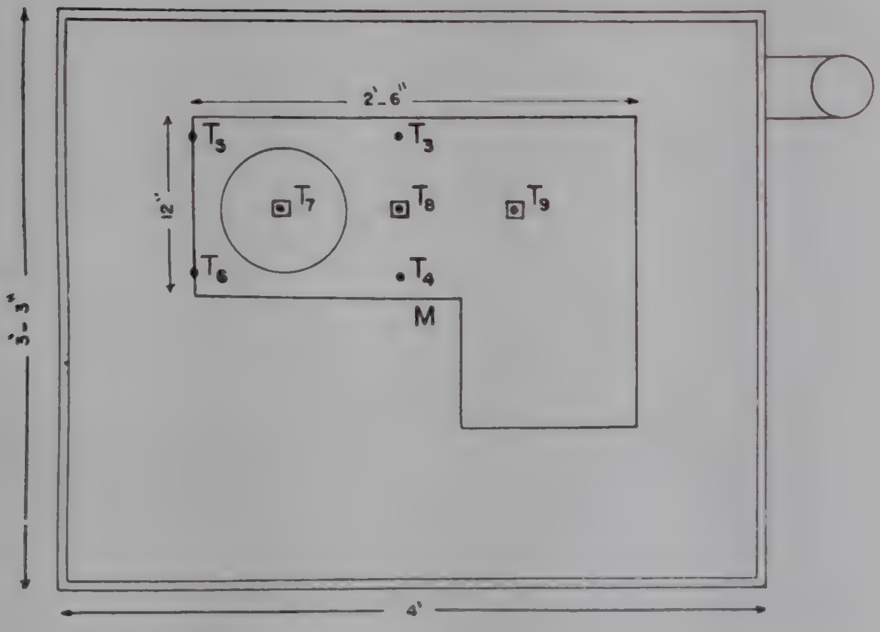
Equipment. The oven used in these studies (Fig. 1) has been constructed with medium-duty refractory bricks. It is provided with two types of 2 ft × 1 ft grates, the clearance between grate bars being $\frac{1}{2}$ in. in one case and $\frac{1}{4}$ in. in the other. In the present series, grate dimensions of 1 ft × 1 ft and 6 in. × 6 in. were used for combustion, the remaining being blocked with bricks. The front part of the oven is fitted with an iron framework with a built-in door provided with adjustable openings for primary air. The top of the oven is covered with a thick metal plate which has an opening of 6 in. diam., directly above the grate. Except during initial filling with fuel, the opening is covered with a metal disc (8 in. diam). The clear height between the grate and metal plate is 10 in. The combustion gases pass side-ways through a passage ($\frac{1}{3}$ft × 1 ft) immediately below the plate to a chimney (8 in. diam × 15$\frac{1}{2}$ ft height). A sliding flap is provided as a damper to control the natural draught. Holes are provided in the brickwork to insert thermocouples at different points in the fuel space. These were sealed during combustion tests. Metal strips were welded on the top of the metal plate at T_7, T_8 and T_9, so that small recesses are provided to insert thermocouples.

Procedure. To start with, the damper in the chimney was set at the desired position and the primary air holes were kept fully open. About 10 g. of cotton waste soaked in kerosene was spread centrally on the grate and covered with air-dry wood chips (1-2 per cent of the weight of semicoke). The cotton waste was lighted and the time noted. After all the kerosene was burnt out, as judged by stoppage of evolution of dark smoke (about 5 min.), a known weight of closely graded semicoke was uniformly spread on the grate and the height of the fuel bed noted. Care was taken to avoid tight packing of the fuel bed and as far as possible a standardized procedure was adopted in making the fuel bed. In some of the earlier tests, lighting was done after filling with semicoke to the desired level.

The metal disc was then kept in position so as to cover the opening and the thermocouple inserted at T_7. Immediately, the time and millivolts for the grate thermocouple T_1 were noted, followed by noting of time and millivolts for the remaining thermocouples. The flue gas temperature was


A = PRIMARY AIR INLET
B = BRICK WORK
C = CHIMNEY
D = DAMPER
G = GRATE
M = METAL PLATE
S = GAS SAMPLING TUBE
T = THERMOCOUPLE
TH = THERMOMETER
D
S
C
M
15.5'
18"
4
TH
$T_{5,6}$
10"
T_2
$T_{3,4}$
9"
12"
T_1
G
2'-9"
1'-6"
9"
B
B
A
1.5"

FRONT ELEVATION


2'-6"
12"
T_5
T_3
T_7
T_8
T_9
T_6
T_4
M
3'-3"
4'

PLAN

Fig. 1—Oven for combustion of semicoke

TABLE 1—VARIABLES STUDIED

VARIABLE	RANGE OF VARIATION		
Total area of grate	1 sq. ft (929 sq. cm.)	0·25 (nominal) (248 sq. cm.)	
Clearance between grate bars, in.	0·5	0·25	0·25
Open grate area, sq. cm.	490	266	57·5
Height of fuel bed, in.	3·5	1,2,3·5,5,6	1,2,3·5,5,6
Damper position $\left(\frac{\text{Open chimney area} \times 100}{\text{Total cross-sectional area of chimney}}\right)$	100,60,8·5	100,60,8·5	100,60,8·5
Size of semicoke, in.	1-1·25	0·5-1·0 (3/4 in.-1 in. 83-88%)	0·5-1·0
Temperature at which air supply was restricted	400-850°C. at grate or centre of fuel chamber		

measured by a thermometer. Thereafter, time and temperature were noted at each point of measurement at intervals of 10-15 min. till the temperature at the centre of the fuel chamber (T_2) dropped to about 150°C.; this sometimes took 10-12 hr. In some of the tests, samples of flue gases were collected from the chimney at different stages of combustion and analysed. In some tests weighed quantities of water were heated in beakers kept at three different places on the top metal plate. The time required for water to start boiling and the weight of water evaporated in a given time were noted.

Variables Studied. The influence of different variables on the course of combustion and temperatures attained at different points in the oven was studied and is presented in Table 1.

RESULTS AND DISCUSSION

Temperature Distribution. Tables 2, 2(A) and 2(B) give, for some typical experiments: (1) maximum temperatures attained at different points in the oven, (2) time required to reach maximum temperatures, and (3) period for which temperatures at the centre of the fuel chamber (T_2), and on top of the plate above the fuel chamber (T_7) could be maintained above specified temperature limits. The variation of temperatures with time are shown in Figs. 2-10, wherein A, B, C denote the stages where the damper position and primary air supply were changed; C_1 denotes clearance between bars, A_1 the total grate area and H the height of fuel bed.

Rise of Temperatures. It is seen from Table 2 ($\frac{1}{2}$ in. grate) that as long as the chimney was kept fully open throughout the test, the temperature just above the grate (T_1) rose to 1000°C. and higher. In several

TABLE 2—TIME-TEMPERATURE DATA ON COMBUSTION OF L.T. SEMICOKE

(Total grate area, 1 sq. ft; clearance between grate bars, 0·5 in.; ht of fuel bed, 3·5 in.; wt of fuel, 6·2 kg.; size of semicoke, 1-1·25 in.)

SERIES No. W-	MAX. TEMP. (°C.) AT				TIME (min.) TO REACH			PERIOD (min.) ABOVE 400°C. AT		ABOVE 300°C. AT		DAMPER* POSITION		P.A. CLOSED AT (°C.)	
	Grate T_1	Centre T_2	Plate T_7	Flue gas	400°C. at grate	Maximum at grate	centre	Centre (T_2)	Plate top (T_7)	Centre (T_2)	Plate top (T_7)	Start	Changed	T_1	T_2
8	1067	873	504	449	11·5	50	60	141	73	168	110	100	no change	1067	851
10	1028	895	499	490	12·5	38	55	137	91	186	122	100	do	840	560
14	1140	872	505	475	13	65	66	140	83	168	114	100	do	775	315
16	855	780	485	342	11	68	105	235	141	270	209	8·5	do	807	427
19	957	745	455	330	15	85	115	253	140	300	218	8·5	do	825	450
21	1032	776	473	336	23·5	101	115	244	123	286	170	8·5	do	1000	800
24	717	641	416	252	5	75**	505	345	35	575	149	8·5	do	600	—
25	800	506	332	70	11	100***	435	453	0	628	197	8·5	do	636	170
27	1027	780	460	360	9	80	137	283	110	346	225	60	8·5	612	143

*Damper position (*see* Table 1).

**When primary air was closed at $T_1=600$°C., T_1 dropped to 465° and again increased to 717°C., total time=75 min. Likewise T_2 dropped from 425° to 175° and again increased to 641°C., total time=505 min.

***Including drop from 636 to 525 and again rise to 800.

NOTE: (*i*) Primary Air (P.A.) portholes were fully open at the commencement of the test. P.A. and damper positions were changed at the temperatures mentioned in the table. (*ii*) In all this series, fuel bed was lighted after filling semicoke.

TABLE 2(A)—TIME-TEMPERATURE DATA ON COMBUSTION OF L.T. SEMICOKE

(Total grate area, 1 sq. ft; clearance between grate bars, 0·25 in.; size of semicoke, 1/2-1 in.)

Series No. K.A-	Fuel bed ht. (in.)	Wt of semi-coke (kg.)	Max. temp. °C.				Time (min.) to reach			Period (min.) Above 400°C.		Period (min.) Above 300°C.		Damper position		P.A. closed	
			Grate (T_1)	Centre (T_2)	Plate (T_7)	Flue gas	400°C. at grate	Maximum at grate	Maximum at centre	Centre (T_2)	Plate top (T_7)	Centre (T_2)	Plate top (T_7)	Start	Chan-ged	T_1, °C.	T_2, °C.
4	3·5	6·25	1164	692	580	270	27	135	210	174	164	199	184	60	8·5	600	80
5	do	do	1120	660	580	286	11	120	180	179	139	204	185	8·5	8·5	520	70
6	do	do	1100	680	564	340	21	120	195	180	157	201	188	8·5	8·5	520	80
7	do	do	1300	724	640	380	24	135	150	108	105	123	132	60	60	520	85
10	do	do	1160	600	508	420	25	135	135	201	182	232	215	60	8·5	1160	600
11	do	do	1100	592	500	300	29	111	255	230	137	267	221	60	8·5	1100	500
14	do	do	832	592	446	340	21	60	120	232	150	275	236	100	0	832	568
														0	60	740	400*
22	do	do	812	644	500	400	32	75	80	200	174	231	207	100	60	780	568
														60	8·5	812	644
														8·5	0	690	590
18	1	2·0	590	520	440	340	26	70	95	34	14	68	45	100	0	480	520
23	2	3·25	880	600	526	390	65	126	135	75	52	106	94	100	60	880	568
														60	8·5	640	590
														8·5	0	295	480
20	5	9·0	906	660	554	360	49·5	145	300	240	166	267	248	100	0	906	568*
														0	60	768	400
														60	0	790	640
21	5	9·0	905	648	576	480	45	103	135	270	237	306	275	100	60	905	568
														60	8·5	765	648
														8·5	0	500	580
26	6	10·5	936	644	476	400	26	165	165	415	325	483	406	100	60	905	568
														60	8·5	936	640
														8·5	0	475	580

*Primary air also changed correspondingly.

NOTE: In experiments 4-11, the tip of the thermocouple T_1 was about 1 in. above the grate; the temperature recorded here is that of the fuel bed and not of the grate. In all other experiments T_1 was kept so that the bed was just above the grate.

TABLE 2B—TIME-TEMPERATURE DATA ON COMBUSTION OF L.T. SEMICOKE

(Total grate area, 0·25 sq. ft; clearance between grate bars, 0·25 in.; size of semicoke, 1/2-1 in.)

Series No. K A-	31	30	27	28	32
Ht of fuel bed, in.	1	2	3·5	5	6
Wt of semicoke, kg.	0·5	1·0	1·5	2·0	2·4
Max. temp., °C. at Grate (T_1)	572	960	904	964	618
Centre (T_2)	172	644	644	644	280
Plate (T_7)	110	354	358	362	134
Flue gas	..	200	180	200	36
Time (min.) to reach 400°C. at grate	16	17	17	17	25
max. at grate	30	45	55	75	195
max. at centre	60	45	60	75	135
Period (min.) above 400°C. at centre	nil	60	158	194	nil
Plate top	nil	nil	nil	nil	nil
300°C. at centre	nil	83	188	238	nil
Plate top	nil	36	44	90	nil
Damper position start	100	100 60 8·5	100 60 8·5	100 60 8·5	100
changed	100	60 8·5 0	60 8·5 0	60 8·5 0	100
P.A. closed at					
T_1°C.	..	925 960 600	904 895 670	940 964 670	..
T_2°C.	..	568 645 530	568 650^a 650^b	568 645 590	..

[a,b]—Time lag between a and b is 50 min. during which T_2 dropped to 570°C. and again increased to 650°C.

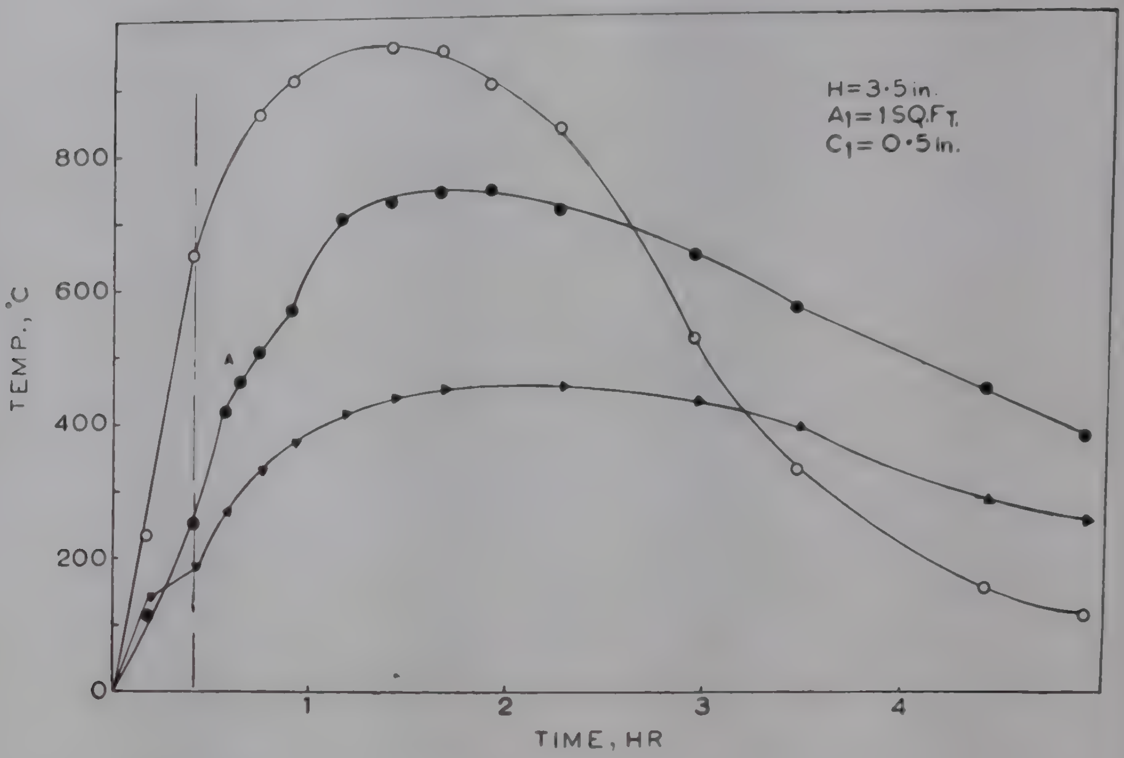


FIG. 2—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

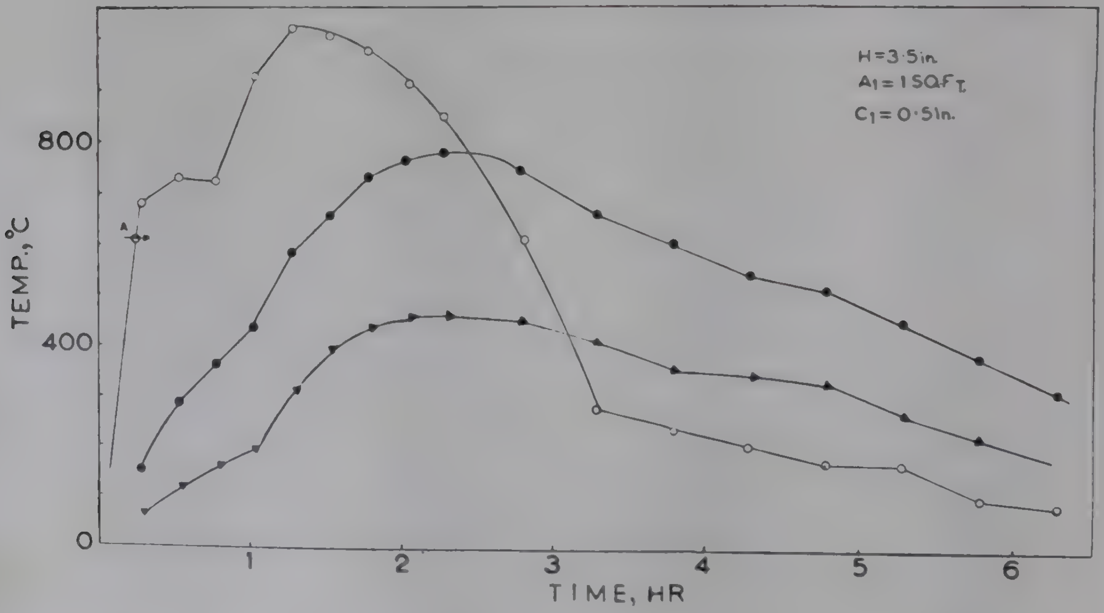


FIG. 3—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

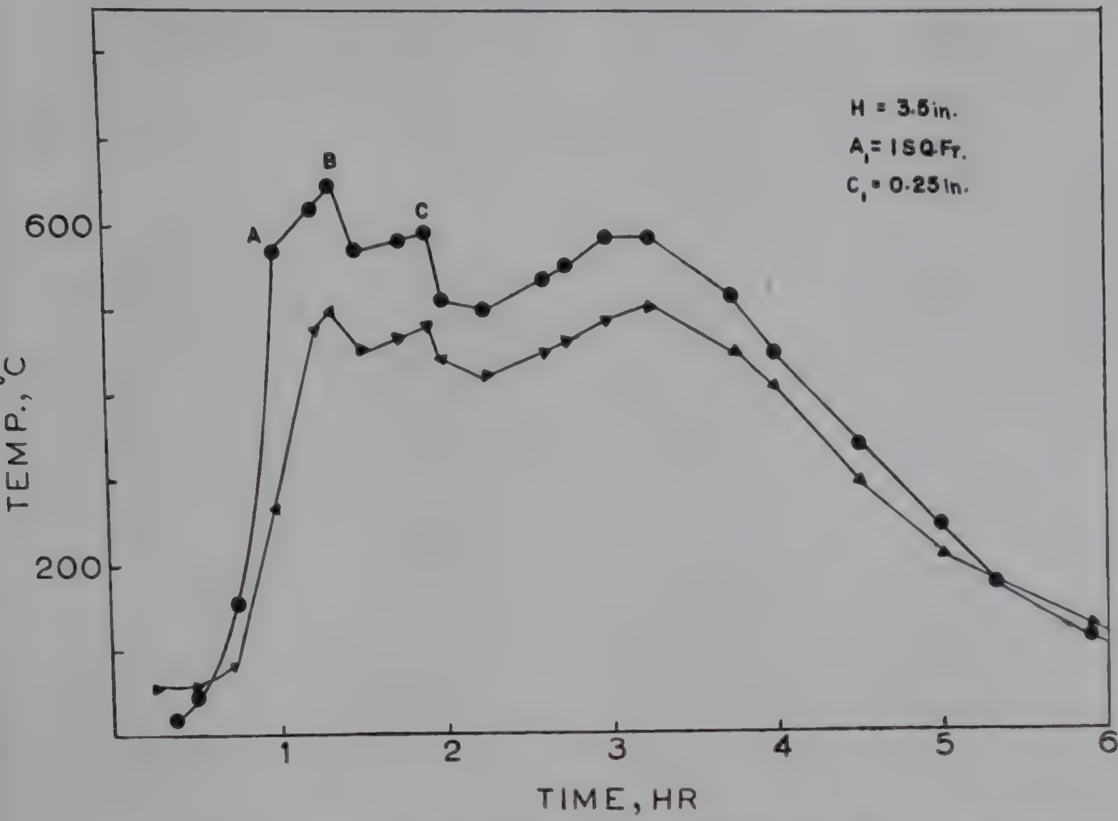


FIG. 4—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

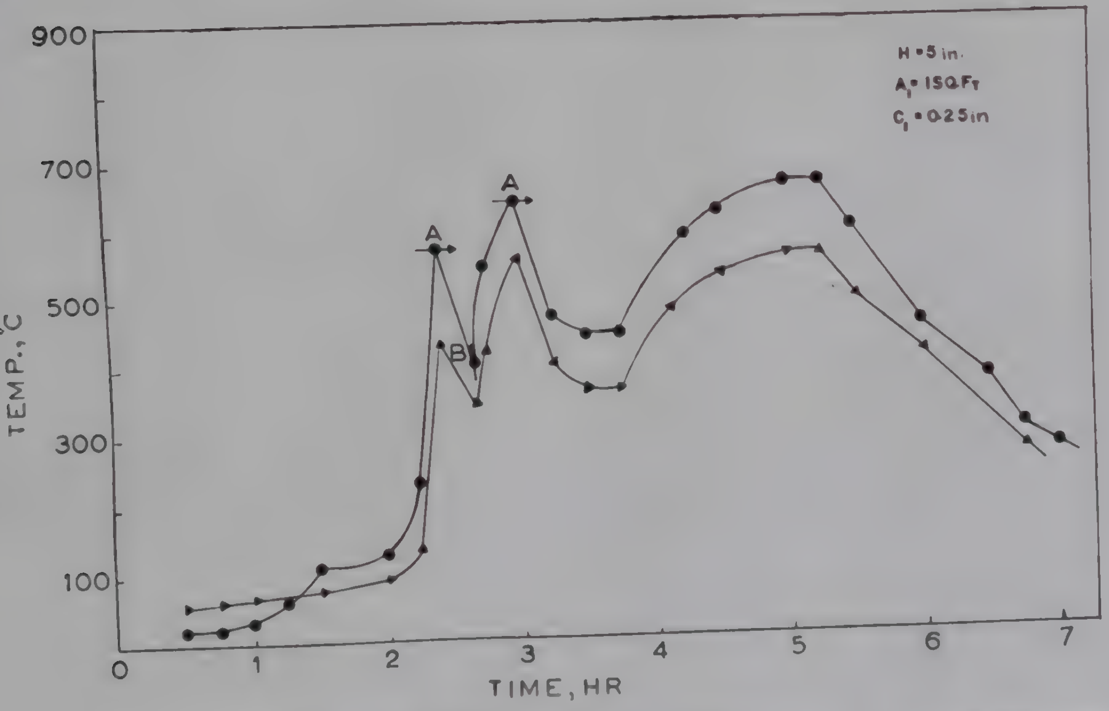


FIG. 5—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

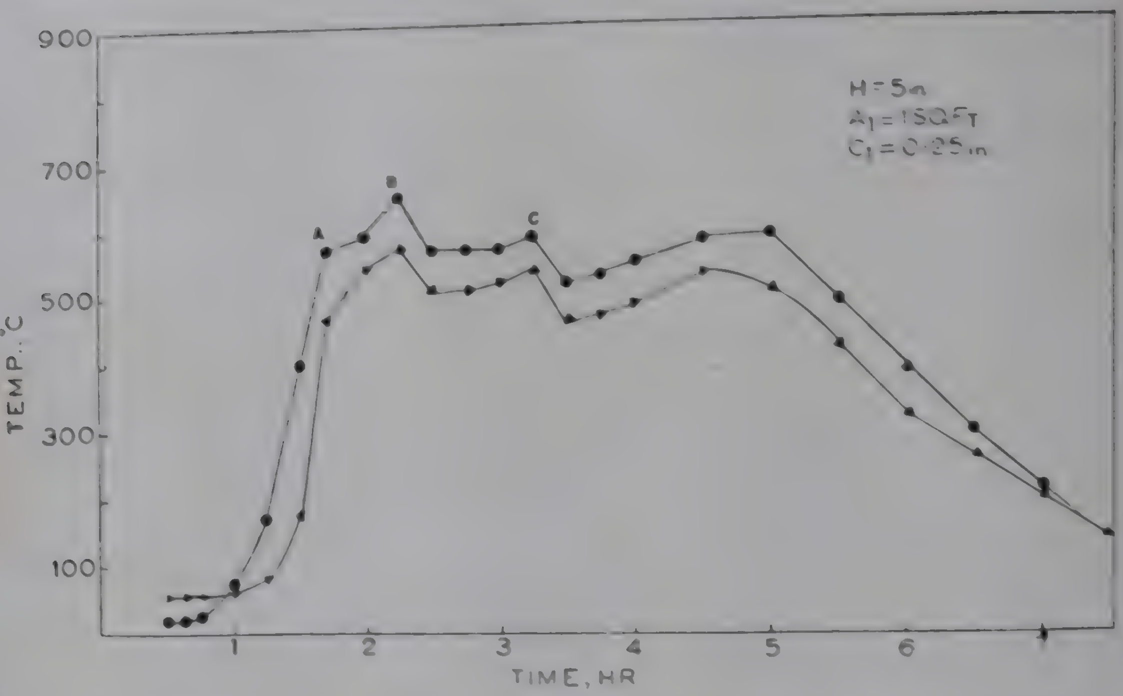


FIG. 6—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

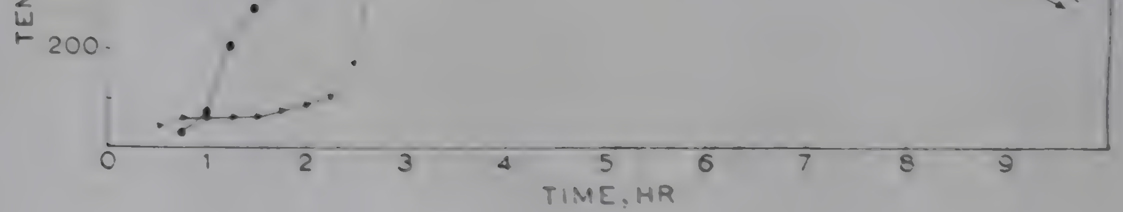


FIG. 7—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

tests it was observed that when T_1 reached about 625-675°C. (Fig. 2), there was a sudden rise in all other temperatures (T_2-T_9, Fig. 1), probably because sufficient carbon monoxide had accumulated above the fuel bed which might have suddenly started burning. In the case of ¼ in. grate, this phenomenon was observed when T_1 was 550-650°C. (Figs. 4-10). The temperatures at the corners of the fuel chamber (T_3-T_6), measured on the same horizontal plane as T_2 were generally 100-200°C. lower than that at T_2.

Lighting Time. Since the ignition temperature of the l.t. coke was found to vary between 380° and 400°C., it was considered that the time required to reach 400°C. at T_1 represented the lighting time. Allowing for some experimental errors due to possible incorrect position of the thermocouple T_1, it can be seen from Tables 2, 2A and 2B, that the lighting time on ½ in. grate was about 10-15 min. This increased to 16-30 min. for the ¼ in. grate; the unusually high time noted in experiments 20, 21 and 23 in Table 2A might have been due to some choke in the fuel bed.

Period Maintaining Above 300°C. Maintenance of a steady temperature at the top plate indicates steady heat output as in an electric hot plate. Temperatures of 400°C. at T_2 and 300°C. at the top plate (T_7) were arbitrarily chosen for comparison of the different tests. The durations above 300°C. and 400°C. at T_7 are much higher with ¼ in. grate than with ½ in. grate, keeping the total grate area and quantities of semicoke the same in both cases. On the other hand, the corresponding periods at T_2 are lower with ¼ in. grate than with ½ in. grate, comparing cases with similar damper positions. This is also reflected by lower plate temperatures and higher centre temperatures on ½ in. grate than on ¼ in. grate. It is probable that the smaller-sized fuel used on ¼ in. grates produced larger quantities of carbon monoxide due to better contact between carbon dioxide from lower layers and carbon in the upper coke layers and that the flames of burning carbon monoxide might be touching the plate bottom. When ½ in. grate is used with larger-sized semicoke, the temperature at T_2 may mostly be due to radiant heat of burning carbon which is always high.

It is further observed that with the low natural draughts (app. 3·0 mm. W.g. maximum) in these studies, the method of throttling the chimney and the grate temperature at which primary air supply is cut off become important. It was found that the hot periods at T_2 can be substantially increased by: (1) starting with a well-throttled chimney and cutting off primary air supply when $T_1 = 600°$-650°C. on a ½ in. grate (Fig. 3; Table 2, No. 24, 25); (2) throttling the chimney in slow stages, particularly when using higher fuel beds.

In the case of reduced grate area and 1/4 in. grate, the hot periods are generally lower, probably due to the reduced quantity of total fuel used.

Assessment of Useful Heat Output. Due to the nonavailability of a thermopile, the temperature-time graphs were used to assess the output of heat at the centre and plate top. In each graph two datum lines were drawn, one at 400°C and the other at 300°C. The areas bounded by the curves and datum lines were computed by a planimeter. The product of the area (sq. cm.) and the scale factor for conversion into centigrade-hours is presented as useful heat units (expressed in centigrade-hours) available at each point of measurement. Some of the data are presented in Table 3. These units were taken to bear a proportionality with the actual available heat expressed as Btu over the total period of combustion.

TABLE 3—USEFUL 'HEAT UNITS' AVAILABLE DURING COMBUSTION OF L. T. SEMICOKE FROM KOTHAGUDEM COAL

Expt No.	Ht. of fuel bed (in.)	Heat units (centigrade-hours) available					
		Above 300°C.			Above 400°C.		
		Grate	Centre	Plate	Grate	Centre	Plate
W- 16	3·5	1139	1422	432	853	999	141
19	,,	2318	1345	391	1998	885	88
21	,,	1078	1444	350	960	998	107
25	,,	1930	1370	62	1273	423	nil
27	,,	1513	1523	356	1204	995	75
K.A- 4	3·5	2465*	868	545	2083*	558	268
5	,,	1895	793	508	1583	473	235
6	,,	1953	885	568	1615	568	278
7	,,	1640	625	493	1363	430	298
8	,,	1673	813	520	1368	468	208
9	,,	1875	828	553	1565	480	248
10	,,	1940	793	498	1548	430	163
14	,,	820	930	394	575	502	74
22	,,	860	840	488	580	480	170
18	1	469	184	79	216	57	9
23	2	575	301	192	390	148	64
20	5	1290	1000	625	785	576	264
21	5	1080	1161	835	754	690	410
26	6	1967	1792	816	1382	1044	202
K.A- 31†	1	128	nil	nil	51	nil	nil
30	2	465	240	21	354	127	nil
27	3·5	842	578	21	592	291	nil
28	5	819	458	25	595	219	nil
32	6	1408	nil	nil	680	nil	nil

*In the experiments 4-10, the heat units at grate represent conditions inside fuel bed (*See* footnote for Table 2).

†Total grate area in experiments 27-32 is 1/4 sq. ft and rest 1 sq. ft.

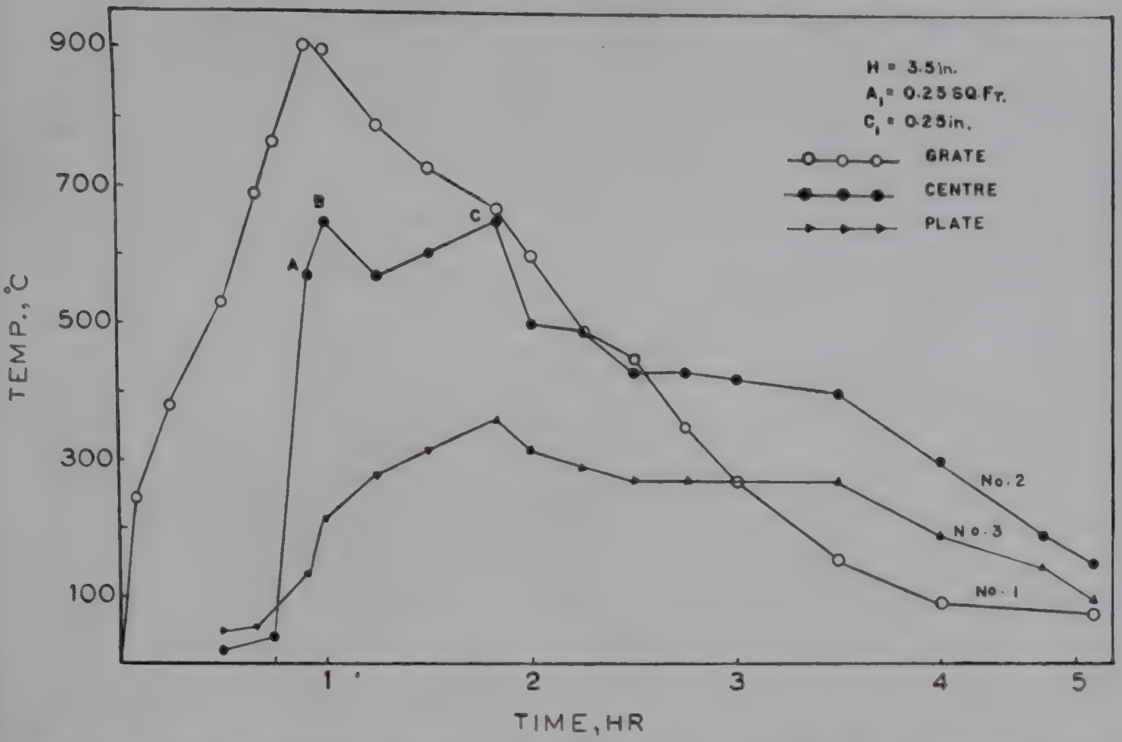


FIG. 8—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

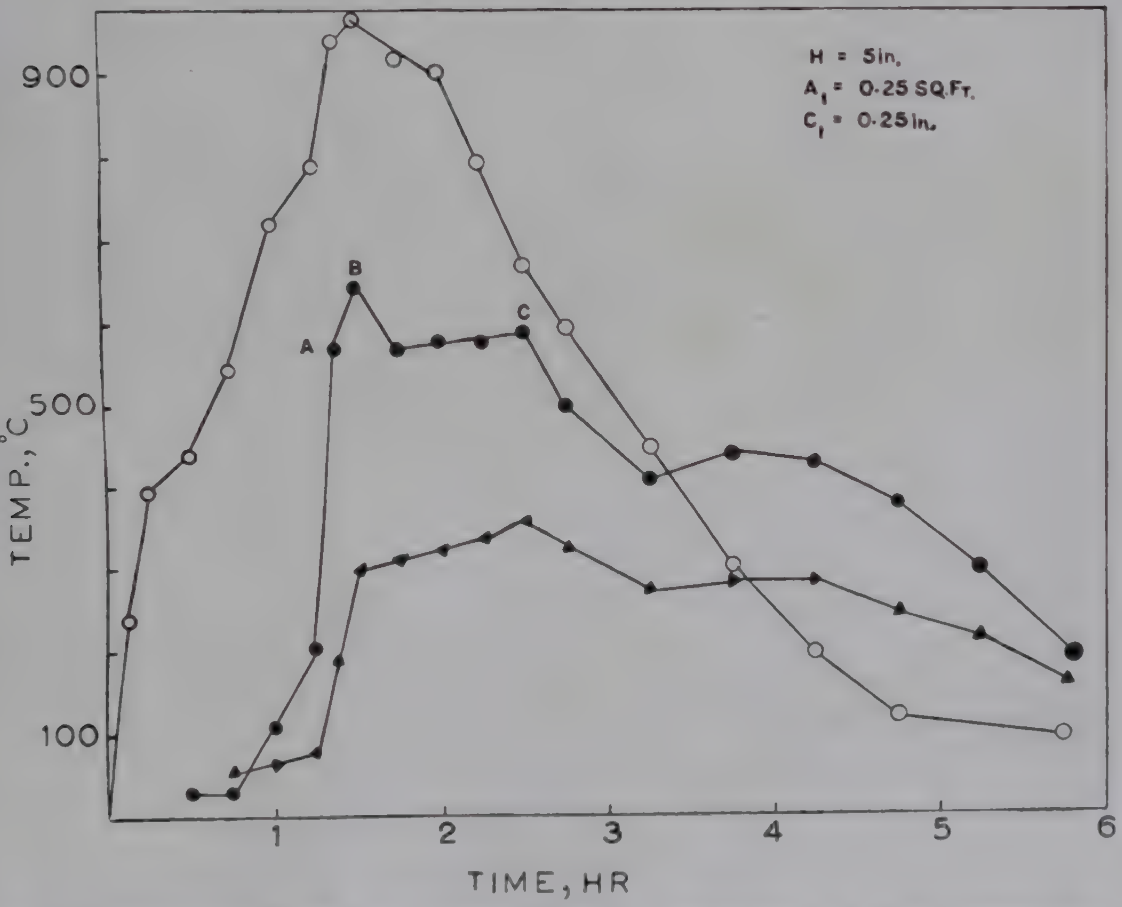


FIG. 9—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

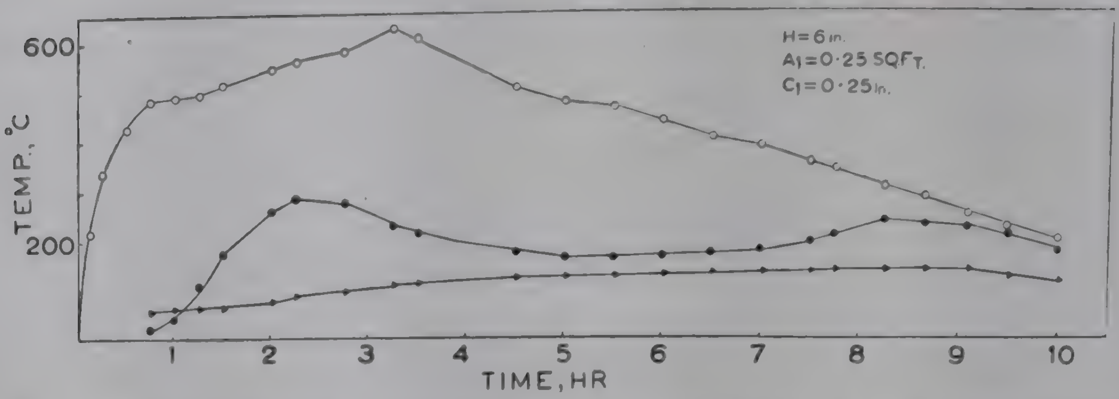


FIG. 10—TIME-TEMPERATURE RELATIONSHIP DURING COMBUSTION OF LOW TEMPERATURE SEMICOKE ON OPEN GRATES

The heat units represent not only the period of maintaining a given heat level but also the intensities reached. It is thus seen that for comparable hot periods, the heat units can vary widely and vice versa (e.g. W-19 and 25, Tables 2 and 3).

The heat units are correlated (Fig. 11) with 'fuel load on grate' expressed as kg. 100 sq. cm. of open grate area; the latter takes into account the total grate area, bed height and weight of fuel used for 1/4 in. clearance between bars. It is seen from Fig. 11 that for each grate size there is an optimum fuel load beyond which the available useful heat units are reduced rapidly due to reduced draught conditions. For a 1/4 sq. ft total grate area having 1/4 in. clearance between bars, the optimum load is found to be 2·8-2·9 kg./100 sq. cm. open area. For larger grate areas this load must be considerably higher.

Fig. 12 shows the correlation between heat units and open grate area for a 3·5 in. bed height. This correlation, plotted on a semi-log paper, takes into account the total grate area, clearance between grate bars and size and weight of fuel used. The heat units obtained in different experiments for a given grate area differ by about 10 per cent which is considered reasonable within the limits of experimental errors involved. The relationship appears linear on a semi-log scale. The equation for the line can be stated as:

$$H=n\times 10^{mA}$$

where H=heat units,
A=open area of the grate (sq. cm.) and
n, m=constants.

From the graph it is found that $n=450$ and m, the slope of the line, is

$$0{\cdot}0012=\log\frac{H_2}{H_1}\Big/\left(A_2-A_1\right).$$

This significance of the value of 'n', the constant at zero open area of the grate appears to be that even if the fuel is taken on a plate and enclosed on all sides except top, it gives a certain minimum amount of heat when once

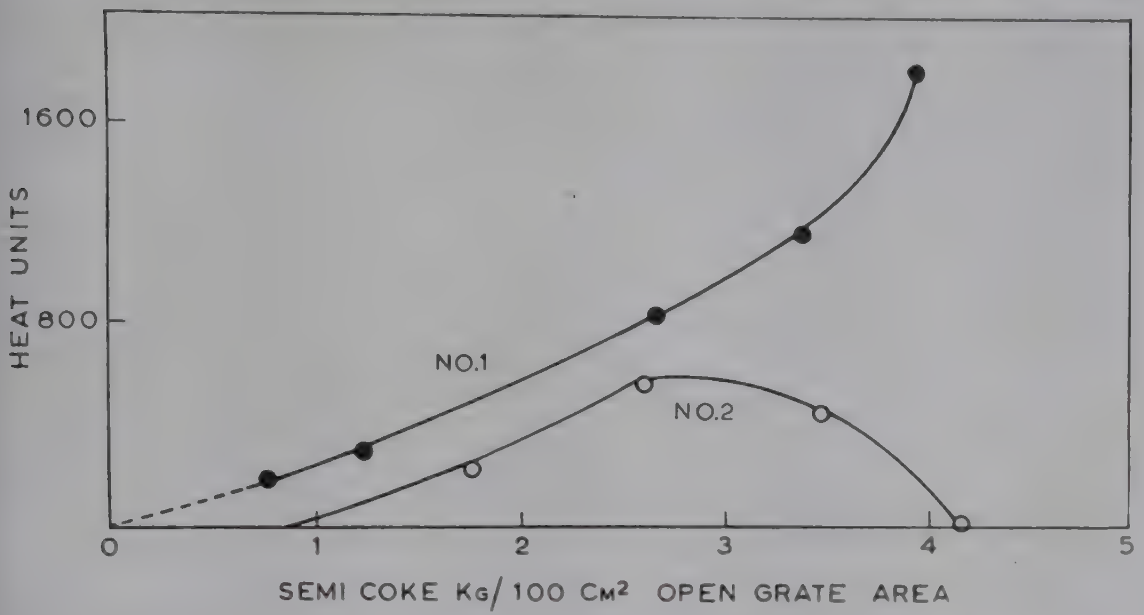


FIG. 11—HEAT EVOLVED DURING COMBUSTION OF SEMICOKE VS FUEL LOAD ON GRATE ($\frac{1}{4}$ IN. CLEARANCE): (No. 1) 1 sq.ft total area; (No. 2) 0.25 sq.ft total area

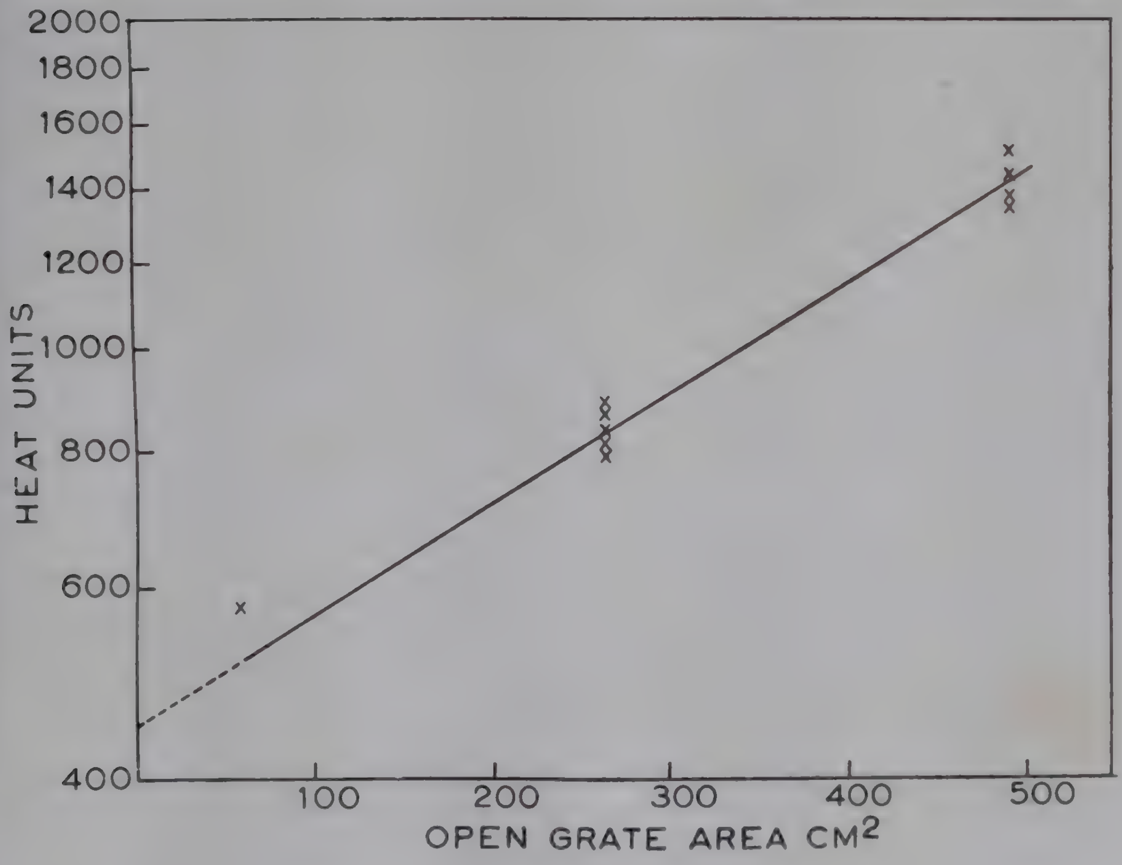


FIG. 12—HEAT EVOLVED DURING COMBUSTION OF SEMICOKE AS A FUNCTION OF OPEN GRATE AREA

it is lighted. The magnitude of this constant may usefully serve as an index of the reactivity, combustibility and related characteristics of the fuel. It is also known in common practice that such reactive fuels like charcoal and wood can be kept burning for sometime in moderately deep trays, without perforations.

Rate of Combustion. In all the tests conducted the fuel was burnt to completion. The residue in all cases was soft ash with no significant unburnt carbon. The amounts of fuel burnt per hour are given below:

TOTAL GRATE AREA (sq. ft)	GRATE CLEARANCE (in.)	COMBUSTION RATE, kg./hr		
		max.	min.	average
1·0	0·5	2·3	1·8	2·1
1·0	0·25	1·6	1·2	1·4
0·25	0·25	0·75	0·34	0·54

It was found that with the 1/2 in. grate, the combustion rate could be reduced to 0·6 1·0 kg./hr by closing the primary air at T_1=600°-650°C. and having reduced draught (No. 24, 25 and 27, Table 2). A bed height of 6 in. on a 1/4 in. grate also reduced the combustion rate. The rate of evaporation of water by boiling water in a glass beaker was of the order of 0·5-0·6 kg./hr with 1 sq. ft and 1/4 in. grate; it was reduced to about 0·2 kg./hr with the 1/4 sq. ft grate.

ACKNOWLEDGEMENT

The authors are deeply grateful to Dr S. Husain Zaheer, for his keen interest in the work and encouragement and to Dr R. Vaidyeswaran for preparation of the first design of the oven used in the tests.

DISCUSSION

Dr S. K. Sircar: The domestic oven described in the paper has no baffles to divert gases upward and downward; it is wasteful to connect directly from fuel bed to the chimney. Further, a full cover plate has been placed on the top. In Calcutta an open type of oven called 'Sarkar Chula' is used without cover. The draft is regulated by combustion itself. What happens if semicoke is burnt in this type of ovens ?

Dr M. G. Krishna: I refer to Fig. 1 wherein it is shown that the cover plate has a hole, 8 in. diam. Normally the vessel is placed on the hole so that the hot gases come in contact with the bottom surface of the vessel. This type of oven, therefore, resembles the open *chula*. The oven used in our studies was constructed mainly to collect data on the influence of various factors such as height of fuel bed, grate area and damper position on the combustion of semicoke.

Between the fuel bed and the chimney a baffle was originally provided. But due to the long time taken by the gases to pass through the baffle, this was subsequently modified. The heat loss in flue gases can be estimated by knowing the temperature and the composition.

Dr S. K. Sircar: There is a type of *chula* in Calcutta known as 'Sarkar Chula.' It is of a similar design with damper but without a hot plate. Certain amount of heat is lost through the flue gases due to chimney draught, but it is preferred because of other advantages such as smoke elimination. How long does it take to light coke in an ordinary open type 'sigree' ?

Dr M. G. Krishna: In an ordinary open *sigree* without chimney, about 8 in. diam. and with 3 in. fuel bed, it takes 10-14 min. to light.

Dr M. S. Iyengar: How is smokeless fuel lighted without producing smoke? If the ordinary housewife uses cowdung cake for 10-15 min. large quantities of smoke will be produced.

Dr M. G. Krishna: Semicoke with 22 per cent ash content is not so easy as charcoal to light. Charcoal can be lighted with paper. In the case of semicoke, usually smaller pieces are placed first on the grate and above them the bigger pieces and lighted with asbestos lighter soaked in kerosene. For 10-15 min. there is smoke. It is a question of preference as to whether one should have smoke for 2 hr or only for 10-15 min. Some users of our semicoke reported that it can be lighted by paper.

Dr S. K. Sircar: I confirm that hard metallurgical coke can be lighted by paper.

Problems in the Origin, Composition and Utilization of Low Temperature Tars

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The purpose of this article is to consider against a background of an increasing production of low temperature tars, with the possibilities that this brings, some of the scientific and technical problems that merit attention. Among these are: the origin of low temperature tars from coal, the composition of different kinds of low temperature tars, analysis of tars, and problems connected with their utilization. Studies made on some of these topics are described here.

The greater interest now being shown in low temperature (l.t.) tars in many countries arises naturally from the increasing, although still comparatively small, production of semicoke, which has been a feature of post-war years in some countries, and of projected development in others. The scientific, technological and economic problems associated with the production and utilization of these tars cannot be isolated, therefore, from what is usually the main purpose of the undertakings, the making of such reactive cokes.

The promise of further large increases in production comes as a result of economic needs and social pressures which vary from country to country. But whatever the main reason prompting an expansion, whether it be the need to conserve for its rightful use on the land the large amounts of animal dung now being used as fuel, or the widespread need to find a substitute for metallurgical coke, or to eke out limited reserves of coking coals, or the desire to promote a cleaner atmosphere, there is the common problem of the more effective utilization of the volatile products.

Although it has been shown, for example, in Britain and France, that, given sufficient research and development, l.t. tars and the aqueous liquors can be processed economically, so far this has been in relation to a comparatively small market, if we set aside the special case of Germany's production of oil from l.t. tars produced from lignite and bituminous coal.

Much of the current research and development work is, naturally, on the immediate utilization of tar and its fractions in bulk form, and on the separation of useful chemicals from it and the aqueous liquor. But it is significant that more fundamental and longer-term studies are receiving increasing attention, for they are the necessary prelude to improvements in utilization, and possibly may lead to the establishment of radically new processes.

Too little is known about l.t. tars made by different methods from coals of different rank and type, and about the origins of and relationship between l. t. tar components. Yet these two interrelated studies can provide information on the variations in the proportions of specific chemical constituents in tars to be expected from a variety of carbonizing conditions. From such studies too, a rational classification of l.t. tars might be developed, and further information obtained on coal structure.

A necessary preliminary to such investigations must be the development of adequate means of analysis. Among such studies are: the detailed separations of tar fractions into individual constituents, and their identification using modern methods; and the subdivision of whole tars into broad groups of chemically related components.

Some of the studies made in this field are presented in this paper.

WHOLE TAR ANALYSIS

A method of analysis of a whole tar based on solvent extraction and adsorption chromatography has been developed[1] and, latterly, standardized[2]. It is given in diagrammatic form in Chart I. The method enables chemically related groups of constituents to be separated quantitatively, and meaningful comparison to be drawn between different tars; it has been used for most of the analyses reported here.

Chromatographic fractions a, b, c, and d, which make up nearly all of the light petroleum-soluble neutrals, are described briefly in Table 1.

TABLE 1—NEUTRAL, LIGHT PETROLEUM-SOLUBLE FRACTIONS IN LOW TEMPERATURE TARS

FRACTION	DESCRIPTION	PREDOMINANT CHEMICAL TYPES
a	White, soft wax, consisting of mixture of oils and waxes	*n*-, *cyclo*- and *iso*-paraffins; *n*, *cyclo*- and *Iso*-olefins
b	Yellow, mobile oil	Alkylated hydroaromatics
c	Dark brown, viscous oil	Alkylated polycyclics, largely naphthalenes
d	Dark brown, viscous oil or semisolid, with characteristic odour	Complex mixture of oxygenated aromatic compounds

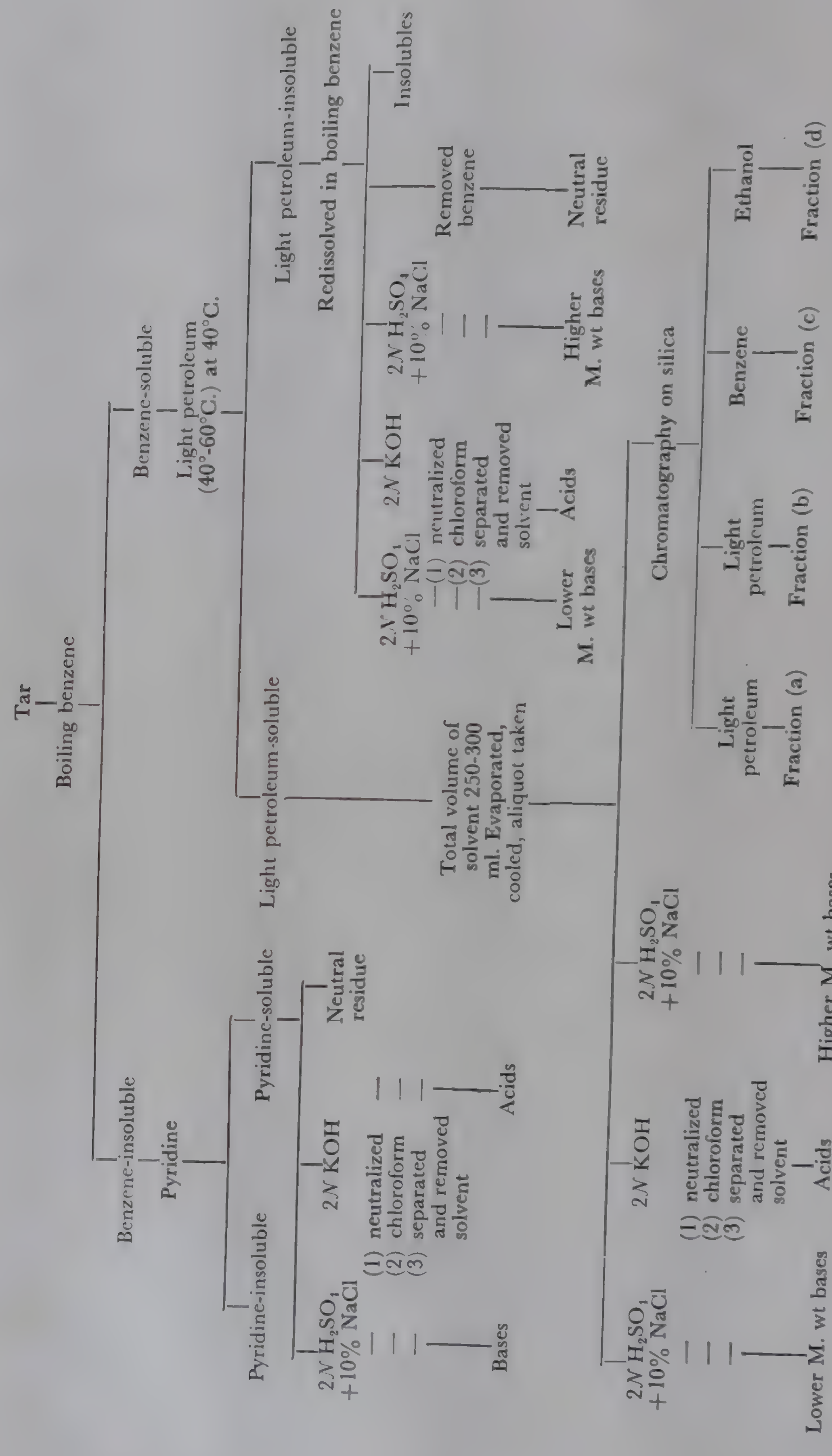
Tar
Boiling benzene
Benzene-insoluble
Pyridine
Pyridine-insoluble
$2N\ H_2SO_4$ +10% NaCl
Bases
$2N$ KOH
(1) neutralized
(2) chloroform
(3) separated and removed solvent
Acids
Pyridine-soluble
Neutral residue
Benzene-soluble
Light petroleum (40°-60°C.) at 40°C.
Light petroleum-soluble
Total volume of solvent 250-300 ml. Evaporated, cooled, aliquot taken
$2N\ H_2SO_4$ +10% NaCl
Lower M. wt bases
$2N$ KOH
(1) neutralized
(2) chloroform
(3) separated and removed solvent
Acids
$2N\ H_2SO_4$ +10% NaCl
Higher M. wt bases
Chromatography on silica
Light petroleum
Fraction (a)
Light petroleum
Fraction (b)
Benzene
Fraction (c)
Ethanol
Fraction (d)
Light petroleum-insoluble
Redissolved in boiling benzene
$2N\ H_2SO_4$ +10% NaCl
Lower M. wt bases
$2N$ KOH
(1) neutralized
(2) chloroform
(3) separated and removed solvent
Acids
$2N\ H_2SO_4$ +10% NaCl
Higher M. wt bases
Removed benzene
Neutral residue
Insolubles

CHART I—GENERAL PROCEDURE OF TAR ANALYSIS

The first three of these are essentially hydrocarbons, although small, variable amounts of other elements, mainly oxygen (O+), are contained, evidently depending on the previous history of the tar and the preparation of the particular fraction.

VARIATIONS IN LOW TEMPERATURE TARS

With Conditions of Carbonization of a Particular Coal

Laboratory Carbonizations. Low temperature tars can be of various degrees of 'primariness', depending on the precise conditions of carbonization[3,4]. As discussed* the most primary product, a true "ur-tar", would coincide with the material of relatively low molecular weight existing in the coal as such, which starts to distil over below the main decomposition temperature of the coal, were it not that implicit in the term 'tar' is its derivation by decomposition of part of the coal substance. Nevertheless, there evidently should exist l.t. tars, poorer in phenols, but richer in the light petroleum-soluble hydrocarbons, the latter being derived partly from the material present as such in the coal and partly from the decomposition of bitumens of the type described*, before the maximum yield of tar has been obtained.

The analyses by the solvent extraction and chromatographic method[2] of four l.t. tars made from a high-volatile, weakly caking, orthobituminous coal (Thoresby) in the Gray-King assay at atmospheric and under reduced (1 cm. Hg) pressures are given in Table 2.

Tar No. 1 (450°C., atmospheric) is, evidently, a tar of the last-named type. It has the largest amount of light petroleum-soluble material, the hydrocarbon fractions a, b and c making up 60·6 per cent of the tar, but the smallest amounts of the more complex fractions, the benzene-insolubles (most complex) and the neutral and acidic benzene-soluble, light petroleum-insolubles, which probably represent stages in the progressive decomposition of parts of the main coal substance. The amount of lower phenols (light petroleum-soluble) in the tar, on the other hand, is quite high on the tar basis.

Carbonization at 450°C. but under reduced pressure (Tar 2) has resulted in a relative (in the tar) and absolute (on the coal basis) increase in the amounts of these more complex materials, but a decrease in the relative amount of simpler phenols, though, absolutely, they remain nearly constant. Evidently, the reduction in pressure has freed the more complex bituminous material and minimized the 'cracking' reactions to the lower phenols.

Tar No. 3 (600°C., atmospheric) lies between these two tars in yield of the complex materials, but the relative and absolute amounts of lower phenols have increased, indicating more degradation than in Tar 2.

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* Discussed under "ORIGIN OF LOW TEMPERATURE TARS" on page 80.

TABLE 2—ANALYSIS OF TARS FROM GRAY-KING ASSAYS OF THORESBY COAL (% by weight)

Tar No.	1		2		3		4	
Carbonization conditions	450°C. ATMOSPHERIC PRESSURE		450°C. REDUCED PRESSURE		600°C. ATMOSPHERIC PRESSURE		600°C. REDUCED PRESSURE	
Basis of analysis (by weight)	% on dry tar	% on d.a.f. coal	% on dry tar	% on d.a.f. coal	% on dry tar	% on d.a.f. coal	% on dry tar	% on d.a.f. coal
Yield of tar (by weight)	—	5·8	—	9·7	—	9·9	—	15·0
1. Benzene-insoluble	(1·23)	(0·07)	(12·12)	(1·17)	(7·72)	(0·76)	(14·98)	(2·25)
Pyridine-insoluble	0·92	0·05	2·78	0·27	1·26	0·12	4·16	0·62
Pyridine-soluble	(0·31)	(0·02)	(9·34)	(0·90)	(6·46)	(0·64)	(10·82)	(1·63)
Bases	0·01	—	0·03	—	0·03	—	0·07	0·01
Acids	0·07	—	1·66	0·16	1·06	0·11	2·17	0·33
Neutral	0·23	0·01	7·65	0·74	5·37	0·53	8·58	1·29
2. Benzene-soluble, light petroleum-insoluble	(15·15)	(0·87)	(23·82)	(2·30)	(18·69)	(1·84)	(24·01)	(3·60)
Bases	0·81	0·05	0·50	0·05	0·45	0·04	0·78	0·12
Acids	5·79	0·33	8·04	0·78	8·04	0·79	9·68	1·45
Neutral	7·46	0·43	13·91	1·34	8·89	0·88	11·40	1·71
Insoluble	1·09	0·06	1·37	0·13	1·31	0·13	2·15	0·32
3. Benzene-soluble, light petroleum-soluble	(79·64)	(4·58)	(60·05)	(5·81)	(69·82)	(6·90)	(56·06)	(8·41)
Bases	0·70	0·04	0·38	0·04	0·75	0·07	0·82	0·12
Acids	14·28	0·82	9·90	0·96	17·71	1·75	16·74	2·51
Neutral	(64·66)	(3·72)	(49·77)	(4·81)	(51·30)	(5·08)	(38·50)	(5·78)
Chromatographic fractions (a)	15·31	0·88	11·91	1·15	11·92	1·18	6·78	1·02
(b)	26·60	1·53	15·07	1·46	16·52	1·64	10·08	1·51
(c)	18·71	1·08	18·81	1·82	18·78	1·86	17·52	2·63
(d)	4·04	0·23	3·98	0·38	4·08	0·40	4·12	0·62
4. Interfacial solids and losses (by difference)	3·98	0·23	4·01	0·39	3·77	0·37	4·95	0·75

The tar made at 600°C. under reduced pressure (No. 4) has the largest amount of complex materials, the simpler phenols having decreased relatively; here again, cracking reactions have been reduced, but not to the same extent as for the tar made by reducing the pressure at 450°C.

Table 3 shows the relative proportions of benzene-insolubles and phenols in the four tars. The reduced effectiveness of vacuum carbonization at 600°C. in countering the cracking of the benzene-insolubles is quite clear.

The total light petroleum-soluble hydrocarbons (chromatographic fractions a, b and c) increase absolutely in the order: 450°C., atmospheric →450°C., reduced pressure →600°C. atmospheric →600°C. reduced pressure. The amounts of hydrocarbons a and b (coal basis) in this order of carbonization are: 2·4, 2·6, 2·8 and 2·5 per cent indicating that they are probably completely released under the mildest conditions of carbonization.

The percentage, of hydrocarbon fraction c (alkylated polycyclics) in the same order are: 1·1, 1·8, 1·9 and 2·6, indicating that further amounts are being released at high temperatures, probably by the decomposition of more complex parts of the coal.

Tars from Carbonization in Small-scale Rexco Retort. Analyses of tars from three carbonizations of the same Thoresby coal at different temperature ranges in a 1 cwt-scale facsimile of the Rexco retort are given in Table 4. Comparing these with the analyses in Table 2, Tar 1 (350-500°C.) corresponds well with Tar 1 (450°C.); the yields of light petroleum-soluble materials on the coal basis, however, are lower, mainly because the yields of hydrocarbons have not been fully realized. Tar 2 (420-510°C.) falls between Tars 1 and 3 (Table 2), as would be expected, but the absolute yields of hydrocarbons, though higher, are still low. In the case of Tar 3 (410-510°C., quicker removal of tar), however, the higher absolute yield of hydrocarbons a and b has been obtained (2·60 per cent), but not that of fraction c. This tar falls between Tars 1 and 3 in every important respect.

TABLE 3—RATIOS OF BENZENE-INSOLUBLES AND PHENOLS IN LABORATORY LOW TEMPERATURE TARS

Tar No.	1		2		3		4	
Carbonization conditions	450°C. ATMOSPHERIC		450°C. REDUCED PRESSURE		600°C. ATMOSPHERIC		600°C. REDUCED PRESSURE	
	a	b	a	b	a	b	a	b
1. Total benzene-insolubles	5·8	1·0	40·3	1·0	23·1	1·0	36·2	1·0
2. Benzene-soluble tar acids:								
Light petroleum-insolubles	27·2	4·7	26·7	0·7	24·0	1·0	23·4	0·7
Light petroleum-solubles	67·0	11·6	33·0	0·8	52·9	2·3	40·4	1·1

a—Percentage of these constituents.
b—Ratio of benzene-soluble tar acids to benzene-insolubles.

TABLE 4—ANALYSIS OF TARS FROM CARBONIZATIONS IN SMALL-SCALE REXCO RETORT

Tar No.	1		2		3	
Carbonization temperature	350-500°C.		420-510°C.		410-510°C. SHORTER RESIDENCE TIME IN RETORT	
Basis of analysis (by weight)	% on dry tar	% on d.a.f. coal	% on dry tar	% on d.a.f. coal	% on dry tar	% on d.a.f. coal
Yield of tar (by weight)	..	2·9	..	6·0	..	7·5
1. Benzene-insoluble	(2·83)	(0·08)	(4·82)	(0·29)	(5·88)	(0·43)
Pyridine-insoluble	2·06	0·06	1·30	0·08	2·98	0·22
Pyridine-soluble	(0·77)	(0·02)	(3·52)	(0·21)	(2·90)	(0·21)
Bases	0·01	..	0·12	..	0·06	..
Acids	0·01	..	0·62	0·04	0·45	0·03
Neutral	0·75	0·02	2·78	0·17	2·39	0·18
2. Benzene-soluble: light petroleum-insoluble	(15·82)	(0·46)	(15·38)	(0·93)	(17·97)	(1·35)
Bases	0·67	0·02	0·49	0·03	1·05	0·08
Acids	5·06	0·15	8·09	0·49	7·05	0·53
Neutral	7·33	0·21	4·83	0·29	8·23	0·62
Insoluble	2·76	0·08	1·97	0·12	1·64	0·12
3. Benzene-soluble: light petroleum-soluble	(75·81)	(2·20)	(73·41)	(4·39)	(71·30)	(5·35)
Bases	0·64	0·02	1·04	0·06	0·57	0·04
Acids	17·70	0·51	19·59	1·17	15·76	1·18
Neutral	(57·47)	(1·67)	(52·78)	(3·16)	(54·97)	(4·13)
Chromatographic fractions (a)	14·43	0·42	10·19	0·61	10·47	0·79
(b)	24·03	0·70	22·08	1·32	24·18	1·81
(c)	15·72	0·46	16·93	1·02	17·01	1·28
(d)	3·19	0·09	3·58	0·21	3·31	0·25
4. Interfacial solids and losses (by difference)	5·54	0·16	6·39	0·39	4·85	0·37

With Rank and Type. The analyses of two l.t. tars made by the down-jet process from high volatile non-caking, and low volatile weakly caking bituminous coals have been reported[1]. Although the yield of tar from the latter was very small, the proportion of neutral, hexane-soluble material was about the same (45·7 per cent on dry tar basis) as in the tar from lower rank coal (45·3 per cent), and the ultimate analyses were similar. Both contained about the same quantity of hydrocarbon wax, separated with butanone at low temperature. The amount of phenols was much lower, and of complex, benzene-insoluble material higher in the higher rank coal.

In l.t. tars from certain perhydrous coals and lignites, the most remarkable differences are in the amounts of the hydrocarbon fractions, a and b. In the waxy tar made by steam distillation at 300-380°C. of Mulgeldie coal (Queensland), a high volatile, perhydrous, drift coal of canneloid type[5], the amount of fraction a was 24·9 per cent on dry tar or 2·1 per cent on dry, ash-free coal basis (compare the corresponding values for the Gray-King assay tars from the orthohydrous coal in Table 2: 6·8-15·3 per cent; 1 per cent). Fraction b (Mulgeldie) made up 17·9 per cent of the dry tar; 1·5 per cent on d.a.f. coal. Thus, the totals for fractions a and b (Mulgeldie) were 42·8 per cent (3·6 per cent) as compared with 16·9-41·9 per cent (2·5 per cent) for the orthohydrous coal tar.

In a Gray-King assay (600°C., atmospheric) of a perhydrous Nigerian lignite[6], the yield of anhydrous tar was 36·4 per cent (d.a.f. coal); it contained 68·9 per cent of fractions a and b. This represented, therefore, a yield of no less than 25·1 per cent on d.a.f. coal.

CLASSIFICATION OF LOW TEMPERATURE TARS

Much more systematic work remains to be done in evaluating and comparing different kinds of whole l.t. tars made from coals of different ranks and types, from lignites of different types, and from petrological components. The following provisional grouping of l.t. tars, based on this and other studies, is put forward.

Class 1. Primary tars made in the lower end of the decomposition temperature range of the coal have the following characteristics: (*a*) yields are low, (*b*) a much larger amount is soluble in light petroleum (about 80 per cent in the cases studied) than for other l.t. tars, (*c*) aliphatic, alicyclic and alkylated, polycyclic aromatic hydrocarbons make up most of the light petroleum solubles, (*d*) the amount of benzene-insolubles, ("primary bitumens", of high oxygen content) is low, as the main part of the coal has not yet been decomposed, and (*e*) low-boiling light oil is present in small quantities and contains aliphatics and aromatics.

Class 2. Primary tars formed during the main decomposition of coal and removed quickly from hot zones have the following characteristics: (*a*) yields are higher, reaching a maximum, (*b*) the amount of benzene-insoluble bitumens is high (up to 15 per cent of a tar in the cases studied), (*c*) the amount of phenols formed is dependent on the degree of decomposition undergone by these thermolabile bitumens, and is, therefore, a function of temperature and residence time, (*d*) the amount of aliphatic and alicyclic hydrocarbons in the tar is relatively lower than in Class 1, but about the same on coal basis, (*e*) the amount of alkylated, polycyclic aromatic hydrocarbons increases with temperature of carbonization within this range of tars, and (*f*) low-boiling light oil is present in small quantity and contains aliphatics and aromatics.

Class 3. L.t. tars which have experienced more severe cracking, e.g. the commercial tars made by external heating of the charge. The characteristics of such tars are: (*a*) yield of tar depends on the amount of cracking it has undergone, but is below the maximum achievable, (*b*) the amount of benzene-insoluble bitumens is low; they may even be absent, (*c*) the amount of lower phenols is correspondingly high, (*d*) dealkylation and other cracking reactions have resulted in the formation of recoverable amounts of phenol, naphthalene and light oil chemicals such as benzene and toluene, and (*e*) more light oil is present with a higher proportion of aromatics, but still more aliphatic than that from a high temperature tar.

It will be seen that this last class of tars merges into those high temperature tars which have a relatively short residence time (e.g. continuous vertical retort tars). It will also be noted that the term "primary" has been applied to the l.t. tars of Classes 1 and 2 only.

ORIGIN OF LOW TEMPERATURE TARS

It has been shown that only a part of the hydrocarbons found in l.t. tars occurs as such in the original coal, as judged by their chromatographic separation from the light petroleum-soluble portions of a dioxan extract of a perhydrous lignite[6], or of the benzene-ethanol extract of the same weakly caking, bituminous coal[7] (Thoresby). The rest of the hydrocarbons arise by thermal decomposition of the coal.

Work in progress on the Thoresby coal (Chart II) has shown that in the l.t. tar obtained by carbonizing the light petroleum-insoluble portion of the benzene-ethanol extract of the coal (analysis in Table 5), the light petroleum-soluble hydrocarbons were similar to those obtained from the coal and the coal tar. Table 6 gives the yields and analyses of the hydrocarbon

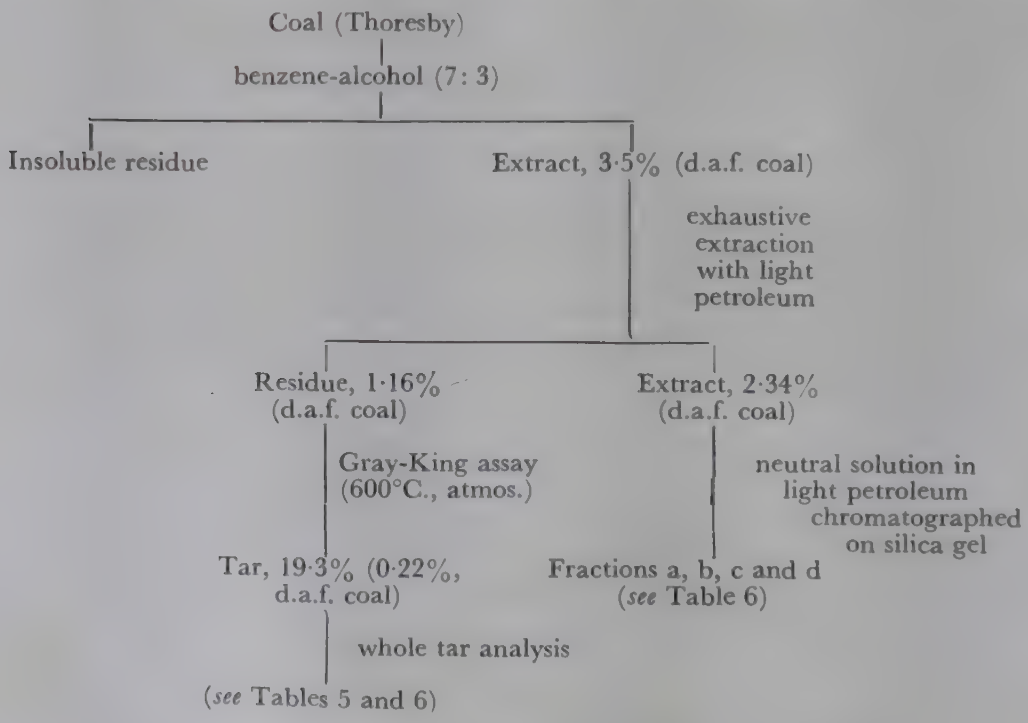
Coal (Thoresby)
benzene-alcohol (7: 3)
Insoluble residue
Extract, 3·5% (d.a.f. coal)
exhaustive extraction with light petroleum
Residue, 1·16% (d.a.f. coal)
Extract, 2·34% (d.a.f. coal)
Gray-King assay (600°C., atmos.)
neutral solution in light petroleum chromatographed on silica gel
Tar, 19·3% (0·22%, d.a.f. coal)
Fractions a, b, c and d (*see* Table 6)
whole tar analysis
(*see* Tables 5 and 6)

CHART II—SCHEME OF TREATMENT OF COAL

TABLE 5—ANALYSIS OF TAR FROM GRAY-KING ASSAY (600°C.) OF LIGHT PETROLEUM-INSOLUBLE PORTION OF COAL EXTRACT

	Wt % on dry tar	% C	% H	n_D^{20}
1. Benzene-insoluble	(2·79)			
Pyridine-insoluble	2·18			
Pyridine-soluble	(0·61)			
Bases	0·01			
Acids	0·11			
Neutral	0·49			
2. Benzene-soluble, light petroleum-insoluble	(27·81)			
Bases	0·04			
Acids	10·21			
Neutral	14·75			
Insoluble	2·81			
3. Benzene-soluble, light petroleum-soluble	(65·33)			
Bases	0·02			
Acids	5·16			
Neutral	(60·15)			
Chromatographic fractions (a)	7·22	85·9	13·8	1·465 (25°C.)
(b)	12·48	85·1	12·9	1·484
(c)	33·60	85·1	9·3	1·581
(d)	6·85	71·9	7·9	..
4. Interfacial solids and losses	4·07			

fractions a, b and c, and of the oxygen-containing fraction d, in this tar (2), in the light petroleum-soluble fraction from the original coal (1), and in a l.t. tar derived from the unextracted coal (3), making the following assumptions:

(*i*) That in the analysis of tar 2 some of the fraction a had run into fraction b, and some of fraction b into fraction c, as judged by the analyses and refractive indexes of b and c. Taking the refractive index of fraction a as found (1·465) and the true values for b and c as 1·530 and 1·610 (the usual values obtained), the yields and analyses have been recalculated.

(*ii*) That the (O+) contents of fractions a, b and c are fortuitous and variable. The analyses for these have been presented on an (O+) free basis.

(*iii*) That all the fractions 'd' have the same (O+) value of 13·8 per cent, i.e. the lowest value obtained of the three fractions.

The three sets of analyses are remarkably similar, strongly suggesting a common ultimate origin of these hydrocarbons, despite the fact that only in part do they exist as such in the coal.

TABLE 6—NEUTRAL, LIGHT PETROLEUM-SOLUBLE FRACTIONS FROM COAL EXTRACT AND COAL TARS

(Corrected values)

Fraction		% Yield on dry extract or tar	% Yield on dry ash-free coal	% C	% H	(O+)	C/H	n_D^{20}
a	1	4·13	0·14	86·1	13·9	—	0·52	1·474 (25°C.)
	2	15·92	0·04	86·2	13·8	—	0·52	1·465 (25°C.)
	3	6·75	0·61	86·2	13·8	—	0·52	1·458 (25°C.)
b	1	3·09	0·11	88·1	11·9	—	0·62	1·534
	2	16·38	0·04	88·5	11·5	—	0·64	1·530
	3	13·43	1·21	88·8	11·2	—	0·66	1·525
c	1	17·32	0·61	91·1	8·9	—	0·85	1·613
	2	21·00	0·05	91·1	8·9	—	0·85	1·610
	3	20·57	1·85	91·3	8·7	—	0·85	1·610
d	1	4·74	0·17	77·2	9·0	13·8	0·72	—
	2	6·85	0·02	77·7	8·5	13·8	0·76	—
	3	5·02	0·45	77·7	8·5	13·8	0·76	—

a, b, c, and d are chromatographic fractions as in Table 1.
1—fraction from light petroleum-soluble portion of benzene-alcohol extract of coal.
2—fraction from l.t. tar by carbonization of light petroleum-insoluble portion of coal extract.
3—fraction from l.t. tar (Rexco Process) from same coal.
(O+)—oxygen and other elements by difference.

The totals of hydrocarbons (fractions a and b only) existing in the coal as such (assuming complete extraction), and from the thermal decomposition of the rest of the coal are given for the lignite and the bituminous coal (Table 7). It will be seen that a much larger proportion of hydrocarbons similar to those surviving coalification is derived from the decomposition of the lignite. In this case the amount of material which could be converted to colloidal, alkali-soluble substances, the so-called "humic acids", was so high (80 per cent d.a.f. coal) that part of it must have been derived from the coalification of the same plant components which probably give rise to the hydrocarbons in the coal (e.g. spores, cuticles, waxes).

Negligible quantities of acidic substances were contained in the light petroleum-soluble portion of the Thoresby coal extract, and only 0·03

TABLE 7—HYDROCARBON FRACTIONS a AND b IN COALS AND GRAY-KING ASSAY TARS (600°C., atmosphere) DERIVED FROM THEM (d.a.f. coal basis)

COAL	% HYDROCARBONS IN LIGHT PETROLEUM-SOLUBLE PORTION OF COAL EXTRACT*	% HYDROCARBONS IN TAR FROM LIGHT PETROLEUM-INSOLUBLE PORTION OF COAL EXTRACT	% HYDROCARBONS IN TAR FROM RESIDUE OF COAL EXTRACTION	% HYDROCARBONS IN TAR FROM UNEXTRACTED COAL
Nigerian lignite	1·1	13·3†	10·7	25·1
Thoresby coal	0·25	0·05	1·52†	1·82

* Dioxan extract from lignite; benzene-alcohol extract from coal.
† By difference.

per cent (d.a.f. coal) of acids in the tar made by carbonization of the light petroleum-insoluble portion of the extract. The maximum yield of tar acids obtained in the carbonization of the original coal (at 600°C. reduced pressure) was 4·3 per cent (d.a.f. coal). Thus, the bulk of the phenols arose from decomposition of the more complex parts of the coal substance.

From the preliminary work reported in this paper, and from previous studies [7,8] the following conclusions on the origin of the more important l.t. tar components are put forward:

(*i*) Hydrocarbons present as such in the coal account for part of those found in the tar.

(*ii*) Most of the hydrocarbons in tar arise by thermal decomposition of the rest of the coal.

(*iii*) It appears from the study of a weakly caking, high volatile bituminous coal that the part of the coal giving rise to the aliphatic and alicyclic hydrocarbons in the tar is easily decomposed, as judged by maximum yields of these (coal basis) obtained on carbonizing at 450°C. with no increase in yields up to 600°C.

(*iv*) The yields of alkylated, polycyclic aromatic hydrocarbons, however, increase in the tars obtained on carbonizing above 450°C., presumably by decomposition of more complex parts of the coal.

(*v*) Primary "bitumens", of high oxygen content, insoluble in organic solvents such as benzene and ether, are obtained by decomposition of the coal substance, the yields increasing for any temperature in the low temperature carbonization range when they are removed from hot zones quickly. They are thermolabile and decompose in stages to form simpler materials. Phenols of different complexities are among the decomposition products in this degradation sequence.

APPLICATIONS TO UTILIZATION

In this section some possible practical applications of these studies are touched on.

Yield and Composition of Tar. The recognition that variations in yield and composition of the tars are wide may have implications for a l.t.c. programme. For example, in some processes (e.g. internal heating of the charge with hot gas; fluidized carbonization) the temperature of carbonization can be varied. It may be expedient in the earlier stages of production of the semicoke, when effective utilization of the tar lags behind to aim at a higher yield of coke and a lower one of tar, by using a lower carbonizing temperature. As the hydrocarbons come off at lower temperatures, the resultant coke should still fall within the category of "smokeless". As research and development increase the potential value of tar, it would be possible to produce more of it at higher temperatures, but of altered composition.

There is less flexibility in carbonization by external heating of the charge. Tars of Class 3 will be produced in more or less the same yield and composition for any one coal.

For the perhydrous coals and lignites, lower temperatures of carbonization have been found to produce high yields of oils and waxes, which could be the principal reason for the undertaking in suitable cases.

Newer Methods of Processing. The existence of already established methods of processing high temperature tars and their distillation fractions, and of markets for the end products, has influenced the development of the low temperature industries. Although it is natural and expedient that large borrowings be thus made, it seems that further consideration needs to be given to l.t. tars as materials in their own right.

The distinctions from high temperature tar are important. Apart from some phenols, l.t. tars and liquors contain fewer individual chemicals in quantity large enough to justify commercial separation, unless specialized uses are found for particular species.

On the other hand, as emerges clearly from whole tar analysis and from the detailed analytical studies mentioned, large fractions of chemically similar type are present, characteristically made up of numerous isomers. The apparently universal occurrence, although in different amounts, of the aliphatic, alicyclic and alkylated polycyclic hydrocarbons in tars made under different conditions and from coals of various ranks and types, has already been noted. The presence of resins of various chemical types, especially of the abundant resinous phenols (resinols) is another constant feature, as is the large amount of phenols of wide-boiling range.

The longer-term possibility thus suggests itself of separating as complete large fractions such potentially valuable components, necessarily by methods other than distillation, e.g. by solvent extraction, drawing widely on the experience in processing petroleum, to which l.t. tars, especially those from perhydrous coals, show many resemblances. Their further subdivision by distillation, further solvent extraction or other means is then possible. Separation of phenols, hydrocarbons and resins on distillation cuts is also possible. Work is in progress on these lines, alongside with that on the more effective utilization of the products.

CONCLUSION

L.t. tar may be the "storehouse of chemicals" of popular or propagandist conception, but its treasures will not fully yield their value unless they are first properly catalogued and then rendered suitable for existing or new markets. Furthermore, the size of the store may set a limit to the sort of process that can be undertaken economically. The separation of tar into fractions by methods additional to distillation is more feasible if large tonnages are available; the pooling of tars to this end may sometimes be possible.

There is a place for a longer-term view in the study, and improvement in the utilization of l.t. tars, implicit in which is their consideration, to a greater extent than hitherto, as materials in their own right.

ACKNOWLEDGEMENT

The author is grateful to Rexco Research and Development Co. Ltd, for the support given to some of the work described, and to G. V. Blunt for many of the carbonizations and tar analyses.

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DISCUSSION

Dr M. G. Krishna: I wish to seek clarification on three points:

1. The amount of benzene-insoluble in the tar obtained at 450 C. and atmospheric pressure is 1·23 per cent, whereas the corresponding value at reduced pressure is 12·1 per cent. By decreasing the pressure, cracking can be expected to be reduced but a higher benzene-insoluble content has been found. Raising the carbonization temperature also increases the benzene-insoluble due to cracking of primary tar. This means that either by decrease in pressure or by increase in temperature of

carbonization, the benzene-insoluble content can be increased. The nature of the benzene-insoluble matters under the two conditions must be different. Can Dr Vahrman throw some light on this ?

2. The ratio, benzene-insolubles/phenols is nearly the same at 450° and 600°C. at reduced pressure (Table 3). It may be that the nature of tar acids is different as a temperature difference of 150°C. is bound to make a great difference. I would like Dr Vahrman to clarify this.
3. I would like to know whether any investigations on the storage properties of the various fractions have been carried out. These properties determine to some extent, the usefulness of l.t. tars for different purposes, as shown by the studies at the C.S.I.R.O., Australia.

Dr M. S. Iyengar: Dr Vahrman stated that part of the hydrocarbon in tar exists in the original coal as such and it withstands coalification. The major portion of the hydrocarbons found in tar results from the decomposition of coal. Has he investigated as to in what form these hydrocarbons exist in coal, in combined or free state ? How do these products differ from the decomposition products when coal is distilled in vacuum ? I am referring to the work of Robb who has studied the decomposition of coal under vacuum using mass spectrographic techniques. He has drawn analogy between this product and the chloroform-soluble fraction of coal heated rapidly to 450°C. Is it the same as the caking principle found in coal ?

What is the mechanism of tar formation ? It differs from rank to rank. It can be suppressed by oxidation or chemical treatment or reaction with sulphur. It can be improved by hydrogenation. Coal is supposed to contain all the types of hydrocarbons—hydro-aromatics, aliphatics and aromatics. Do all these contribute to tar formation or only one specific component ? Regarding the oxygen in coal, 10 per cent of the total oxygen is known to exist as phenols and by distillation, only part of this fraction is released. Large amounts of oxygen-containing compounds go to form water but still considerable amount of oxygen is left out which would be available for tar acid formation.

Dr H. S. Rao: What exactly is meant by hydro-aromaticity ? Does it refer to tetralin type or decalin type ?

Dr M. Vahrman: First, I refer to Dr Krishna's questions. We are, in fact, dealing with different kinds of benzene-insoluble material, and hence one has to be careful to consider the solubility of this and other fractions in conjunction with other analytical and structural information on them.

The benzene-insolubles in high temperature tars ("free carbon") are high in carbon and low in other elements. In the first two classes of l.t. tars mentioned in the paper, the benzene-insolubles, representing fairly primary fragments of part of the coal structure, have a higher oxygen content and hydrogen content and are mainly fusible. In the primary tar of Class 1 the benzene-insoluble portion is least because much of the coal still remains to be decomposed. The increase of these materials in Class 2 is associated with the main phase of decomposition of the coal, the tar vapours bearing these fairly primary fragments being removed quickly from hot zones. In Class 3, the amount of benzene-insoluble material is low or even absent because a balance has been reached between the decomposition of the bitumens and the formation of benzene-insoluble materials from them. With increase of temperature and/or decrease in residence time, the benzene-insoluble materials of high carbon content characteristic of high temperature tars, appear and increase owing to the carbonization of other tar components.

Much more work needs to be done on the variation with carbonization conditions of the nature of the acidic components of tar, for there is very little information available. On the storage properties, chromatographic fractions (*a*), (*b*) and (*c*) are not greatly affected by oxidation, but fraction (*d*) (oxygen-containing) tends to oxidize and polymerize. In general, on storage, more benzene-insolubles and light petroleum-insolubles develop from fractions formerly soluble in these solvents; oxygen-containing components seem to be the most affected.

The nature of tar formation and the other points raised by Dr Iyengar are intriguing. There can now be little doubt that materials existing in the coal as such distil over relatively unchanged in the production of primary tars, and may even survive in other tars to varying degrees, depending on the carbonizing conditions. Three fairly recent pieces of work support this view: that of Benzole Producers Ltd. in the U.K. on the presence of benzene and its homologues and of homologous series of aliphatic hydrocarbons in coal (analysed by gas-liquid chromatography); that of Robb and coworkers at Birmingham University on the detection by mass spectography of homologous series of hydrocarbons, paraffinic and aromatic, liberated from coal before its main decomposition, phenols appearing to be decomposition products; and our own work on coal extracts and coal tars which has shown that the hydrocarbon series in both were very similar, and that the bulk of the phenols were of secondary origin, being formed from the decomposition of 'primary' (benzene-insoluble) bitumens. I would refer you to the paper itself for further detail.

This is very much 'work in progress', and it is hoped that a clearer and more detailed picture will emerge over the next few years.

I have used the term 'hydroaromatic' as an omnibus word, I hope not incorrectly, to cover hydrogenated six-membered carbocyclic systems.

Separation of the Constituents of Low Temperature Lignite Tar by Solvent Extraction

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A quantitative analysis of low temperature tar obtained from the lignite of South Arcot based on solvent extraction is described. The properties and the infra-red spectrum of the wax and of the neutral oil are given. The composition of this tar is compared with that of the tar produced at the same temperature from bituminous coals. Solvent separation reveals that the lignite tar might prove to be a good source for paraffin wax and neutral oil.

Solvent extraction is more advantageous to evaluate low temperature (l.t.) coal tars than the standard procedures of the distillation assay[1]. In the latter case the tar particularly l.t. tar undergoes thermal decomposition, oxidation and polymerization. Thus the standard method does not give the composition of the original tar but of the distillation products of the tar. A considerable portion of the tar remains unassessed as pitch. In the case of solvent extraction, the whole tar is analysed, pitch is avoided, maximum temperature is only that needed for the evaporation of the low boiling solvents used, and homogeneous classes of chemicals can be separated to a greater extent than by distillation methods.

EXPERIMENTAL

L.t. tar obtained from kilogram assays of the South Arcot lignite was analysed by the following solvent extraction method. The physical properties of the tar investigated are given in Table 1. The results of the fractional distillation of the tar are shown in Table 2.

TABLE 1—PHYSICAL PROPERTIES OF TAR

Carbonization temp., °C.	600
Sp. gr. of dry tar	0·958
Moisture, % (Dean and Stark)	12·94
Toluene insoluble, %	3·18

TABLE 2—FRACTIONAL DISTILLATION OF TAR

TEMP. RANGE, °C.	DISTILLATE %	CUMULATIVE %
Up to 170°	1·50	1·50
170–235°	8·75	10·25
235–270°	8·66	18·91
270–355°	46·04	64·95
Residue and losses	35·05	100·00

The solvent extraction process adopted is represented diagrammatically in Chart I.

The moisture content was estimated by the Dean and Stark method on a separate representative sample.

The sample of tar (20 g.) was extracted with petroleum ether (40-60°C.) several times until the latter dissolved no more. The residue was thoroughly washed with petroleum ether and dried free of the solvent.

PETROLEUM EXTRACT

The petroleum ether solution was shaken with 5 per cent sodium hydroxide solution in a separating funnel. The aqueous layer contained the acidic and phenolic components. In the interphase a polymerized product was obtained. The aqueous layer was separated, saturated with carbon dioxide and then extracted with ethyl ether. From the ethereal solution phenols were isolated and weighed. The aqueous layer left behind was acidified and extracted with ether, and carboxylic acids determined.

The petroleum ether solution freed of acidic components was treated with 5 per cent sulphuric acid solution in a separating funnel. The aqueous layer was separated, neutralized and the bases were isolated by extraction with ether.

The neutral components—neutral oils and waxes present in the petroleum ether layer were freed of the solvent, dissolved in acetone and cooled in a freezing mixture. The precipitated waxes were filtered off in a Buchner funnel, washed with cold acetone, dried at low temperature under vacuum and weighed. The neutral oils from the acetone solution were freed of the solvent and weighed.

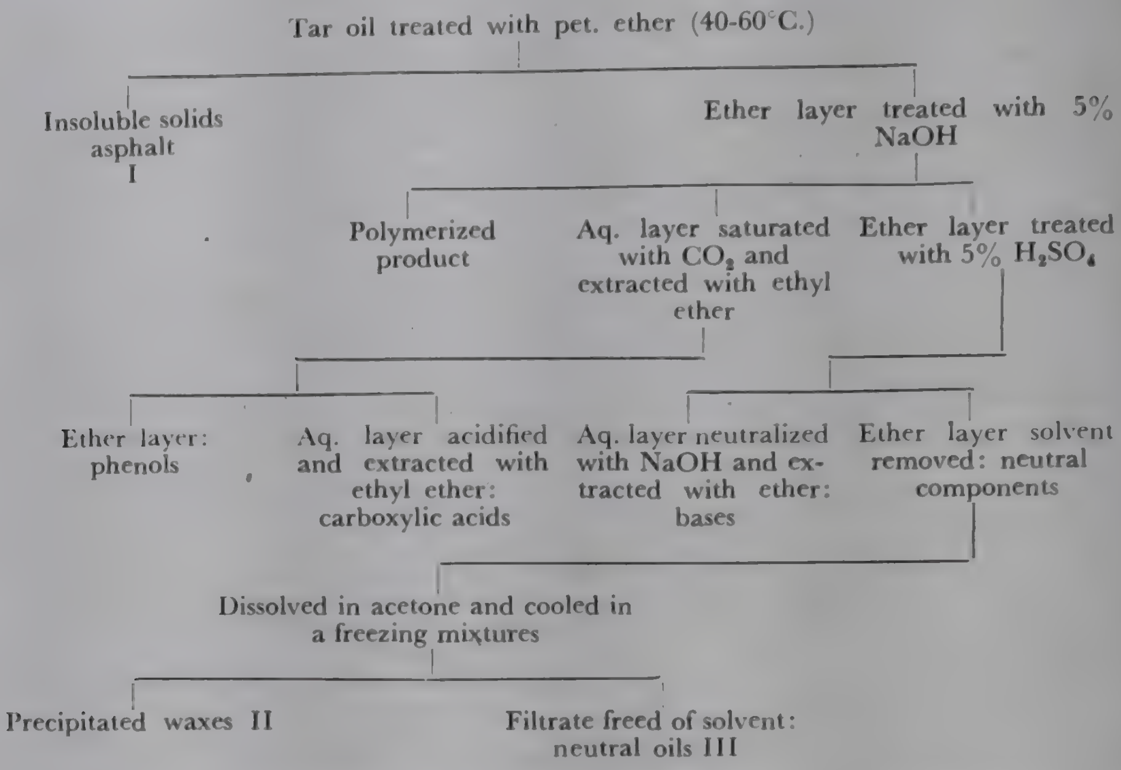
Tar oil treated with pet. ether (40-60°C.)
Insoluble solids asphalt I
Ether layer treated with 5% NaOH
Polymerized product
Aq. layer saturated with CO₂ and extracted with ethyl ether
Ether layer treated with 5% H₂SO₄
Ether layer: phenols
Aq. layer acidified and extracted with ethyl ether: carboxylic acids
Aq. layer neutralized with NaOH and extracted with ether: bases
Ether layer solvent removed: neutral components
Dissolved in acetone and cooled in a freezing mixtures
Precipitated waxes II
Filtrate freed of solvent: neutral oils III

CHART I—FLOWSHEET OF SOLVENT CONTRACTION PROCESS

PETROLEUM ETHER-INSOLUBLE

Petroleum ether-insoluble was treated with small quantities of benzene and 50 per cent sodium hydroxide solution until alkaline and extracted with benzene. The neutral asphaltenes, residue containing carbenes and free carbon, asphaltone phenols and asphaltene acids were estimated as before according to the scheme illustrated in Chart II.

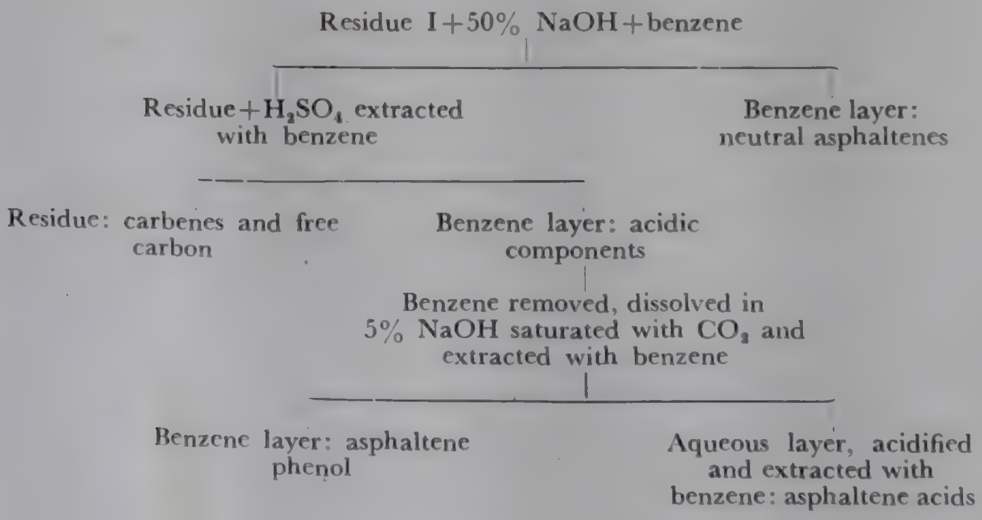
Residue I+50% NaOH+benzene
Residue+H₂SO₄ extracted with benzene
Benzene layer: neutral asphaltenes
Residue: carbenes and free carbon
Benzene layer: acidic components
Benzene removed, dissolved in 5% NaOH saturated with CO₂ and extracted with benzene
Benzene layer: asphaltene phenol
Aqueous layer, acidified and extracted with benzene: asphaltene acids

CHART II—ANALYSIS OF ASPHALT

TABLE 3—INFRA-RED SPECTRUM OF THE WAX

REGION OF SPECTRUM ABSORPTION, microns	ASSIGNMENT	REMARKS
3·45, 3·53	C—H stretching	Strong intensity
5·71, 5·81	C=O	Very low intensity—may be acetone impurity
6·81, 6·84, 7·26	C—H deformation	Strong intensity
8·56, 10·13, 10·59, 11·02, 11·28		Intensity very low indicating a trace of trans double bond may be due to solvent impurity

Table 3 shows the results of the analysis of the lignite tar oil along with the analyses of typical tar oils from peat[2], bituminous coal[3] and Rexco Process[4].

The wax isolated as above had the following properties: C=84·89; H=14·52; melting point, 54°C.; molecular weight by Rasts Method, 493. There was no uptake of hydrogen when hydrogenated. The recrystallized products had a melting point range of 60 to 64°C. The infra-red spectrum of the wax (Table 3) showed only the typical bands for a saturated hydrocarbon and very few other significant features.

CHROMATOGRAPHIC SEPARATION OF THE NEUTRAL OIL

The neutral oil freed of wax was dissolved in petroleum ether and the resulting solution was run into a glass column filled with silica gel of chromatographic grade. A dark band was formed at the top of the column. The chromatogram was eluted with petroleum ether which was found to be a poor eluant. By eluting with benzene a yellow solution was obtained, which after the removal of the solvent yielded a yellow liquid with green fluorescence. The dark band was not affected by elution with benzene. When eluted with acetone the whole band moved and was completely removed. The acetone solution gave a red solid substance melting at 50°C. The ultimate analyses of these fractions are given in Table 4.

The infra-red spectrum of the neutral oil (Table 5) showed strong intensity of absorption in the region for aliphatic and aromatic hydrocarbons.

The ultra-violet absorption spectra of these two fractions gave a maximum at 2300 Å with E^{1}_{1}, 550, 2340 Å with E^{1}_{1}, 240 and 2560 Å with E^{1}_{1} 165 which indicated the presence of conjugated double bonds in both the fractions and probably phenyl groups.

TABLE 4—CHROMATOGRAPHIC SEPARATION OF NEUTRAL OILS

SOLVENT	%	COMPOSITION, %		
		C	H	O (by difference)
Benzene	76·40	85·98	10·44	3·58
Acetone	6·65	74·06	7·89	18·05
Losses	16·95	..	..	..

TABLE 5—INFRA-RED SPECTRUM OF THE NEUTRAL OIL

ABSORPTION, microns	ASSIGNMENT	INTENSITY
2·96	OH	Weak
3·45, 3·55	C—H stretching	Strong
5·86	C=O	Medium
6·11, 6·24	C=O	Medium
6·89, 7·30	C—H deformation	Strong

TABLE 6—ANALYSIS OF TAR OIL BY SOLVENT EXTRACTION

(dry basis)

	COMPONENTS	PEAT	SOUTH ARCOT LIGNITE	REXCO	BITUMINOUS COAL
I	Colloids	(17·7)	(16·60)	(17·30)	(10·40)
	Neutral asphaltene	6·5	5·54	7·68	
	Asphaltene phenols	9·1	1·99	7·98	
	Asphaltene acids	0·6	1·72		
	Carbenes and free carbon	1·5	7·35	1·16	
II	Crystalloids	(54·6)	(77·35)	(67·00)	(88·82)
	Phenols	8·6	7·42	17·80	30·30
	Carboxylic acids	0·5	1·67		0·22
	Bases	1·1	1·86	1·92	2·70
	Waxes	27·1	10·43	(47·28)	2·50
	Neutral oils	(17·3)	(55·97)		(53·10)
	Chromatographic fractions				
	(*a*)	..	43·00	42·90	..
	(*b*)	..	3·82	4·20	..
III	Interfacial solids and losses	(27·7)	(6·05)	(14·00)	(0·78)

DISCUSSION

The results of the analysis (Table 6) indicate that the whole of the tar can be accounted for and a detailed comparative study of tars can be made.

The percentage of tar acids in lignite tar is much less than that in l.t. coal tar but the wax content of lignite tar is four times that of coal tar, while the corresponding value for peat tar is more than double that of lignite tar. The neutral oil content in lignite tar and bituminous coal tar is three times that of peat tar.

The characteristics of the neutral oil seem to be the same as those of the neutral fractions isolated by Blunt and Vahrman[4] from coal tar.

Solvent separation reveals that lignite tar might prove to be a good source for paraffin wax. The neutral oil yield (yield more than 50 per cent) will find use in the manufacture of synthetic petrol and as a raw material for production of fatty acids by oxidation.

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The Chemical Composition of Light Oils from L. T. C. of Polish Bituminous and Brown Coals

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Light oils obtained during the carbonization of a bituminous coal at 750 C. in a Lurgi oven and two brown coals in a semi-industrial oven at 520-530 C. have been examined for elementary analysis, physico-chemical properties, nonhydrous carbon and hydrocarbon groups. Yield of light oil from brown coals amounted to 0 5 per cent on dry coal basis and 7·8 per cent on tar basis. The light oil from brown coal contained 21-24 per cent of phenols while that from bituminous coal contained 12 per cent only. The neutral portion of the light oil contained 52-54 per cent of aromatic hydrocarbons.

The properties of solid residues of low temperature carbonization (l.t.c.) of brown coals and partly of peats have been previously reported[1]. However, the characterization of the low temperature (l.t.) tars has not been extensively studied. This work is the first of a series of investigations on l.t. tars and their fractions.

THE PREPARATION OF MATERIALS FOR RESEARCH*

The light oil from bituminous coal (79·0 C; 4·9 H) was obtained by carbonizing at 750°C. in a Lurgi type industrial carbonization plant. The light oils from two samples of brown coals (Code Nos. Bl-45 and Bl-64) from a colliery in the Poznan district have been obtained by carbonization at 520-530° in a semi-industrial oven described in a previous paper[2].

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*This work has been done in collaboration with Mrs H. Urbanik.

The brown coal B1-45 was prepared by briquetting under a pressure of 2500 kg./sq. cm. The brown coal B1-64 obtained in form of heating briquettes was reduced to lumps of *c.* 5 cm. The ultimate analysis of these coals is given in Table 1.

Carbonization was conducted at a temperature of 520-530°C. for *c.* 12 hr. The properties of the chars and tars obtained are shown in Tables 2 and 3.

The tars after dehydration were distilled into three fractions: (*a*) below 200°C., (*b*) 200–280°C., (*c*) above 280°C. The yields of respective fractions are presented in Table 4.

TABLE 1—ANALYSIS OF BROWN COALS

SAMPLE	MOISTURE %	ASH (dry basis) %	% ASH-FREE DRY COAL					V. M. DRY BASIS %	EXTRACTED MATTER (dry basis) %
			C (dry ash-free basis)	H	S	N	O+ errors		
B1-45	13·0	11·8	66·0	5·5	0·1	0·6	27·8	50·6	11·5
B1-64	13·2	17·1	76·6	5·7	0·4	0·4	25·9	49·4	10·1

TABLE 2—ANALYSIS OF CHARS

SAMPLE	MOISTURE %	ASH (dry basis) %	V.M. (dry basis) %	C (dry, ash-free basis)	H	O+S+N+ ERRORS %
B1-45	2·9	23·9	15·3	86·5	3·0	10·5
B1-64	4·7	31·7	21·7	—	—	—

TABLE 3—ANALYSIS OF TARS

SAMPLE	C	H	H/C ATOMIC RATIO
B1-45	81·9	9·8	1·44
B1-64	82·7	10·1	1·46

TABLE 4—THE YIELD OF FRACTIONS

SAMPLE	BELOW 200°C. % TAR ON DRY COAL		200-280°C. % TAR ON DRY COAL		ABOVE 280°+LOSS % TAR ON DRY COAL	
B1-45	7·8	0·5	19·6	1·2	72·6	4·3
B1-64	7·6	0·5	18·0	1·2	74·4	5·2

The results of investigations on fraction boiling below 200° are described in this work.

INVESTIGATIONS ON LIGHT OILS

The physicochemical properties and ultimate analysis of the fraction distilling below 200° are listed in Table 5.

The resin content in the light oils (Table 6) was estimated by means of "glass dish" method[3].

The non-hydrocarbon components were removed from light oils by conventional methods. Light oils No. 45 and 64 contained 21·3 and 23·7 per cent of phenols and 1·2 and 1·4 per cent of pyridine bases respectively. The content of phenols in light oil No. 65 was only 12·0 per cent and that of pyridine bases 1·0 per cent.

TABLE 5—PROPERTIES OF LIGHT OIL AND GASOLINE

SAMPLE* No.	d_4^{20}	n_d^{20}	VISCOSITY (20°C.) IN CENTI-POISES	MOL. WT	ULTIMATE ANALYSIS %				H/C ATOMIC RATIO
					C	H	S	N+O+ errors	
45	0·8782	1·48019	1·3938	130	81·5	9·9	0·3	8·3	1·46
64	0·8980	1·48634	1·4655	135	80·5	9·5	1·4	8·6	1·42
65	0·8261	1·46295	0·7461	119	82·1	10·6	0·8	6·5	1·55
89	0·7400	1·41923	0·6684	140	85·2	14·2	0·1	0·5	2·00

*No. 45 and 64—light oils corresponding to the brown coals B1-45 and B1-64; No. 65—light oil from the bituminous coal; No. 89—gasoline from crude oil (for comparison).

TABLE 6—THE RESIN CONTENT OF LIGHT OILS

SAMPLE No.	RESIN, mg./100 ml.
45	739·0
64	591·0
65	627·4

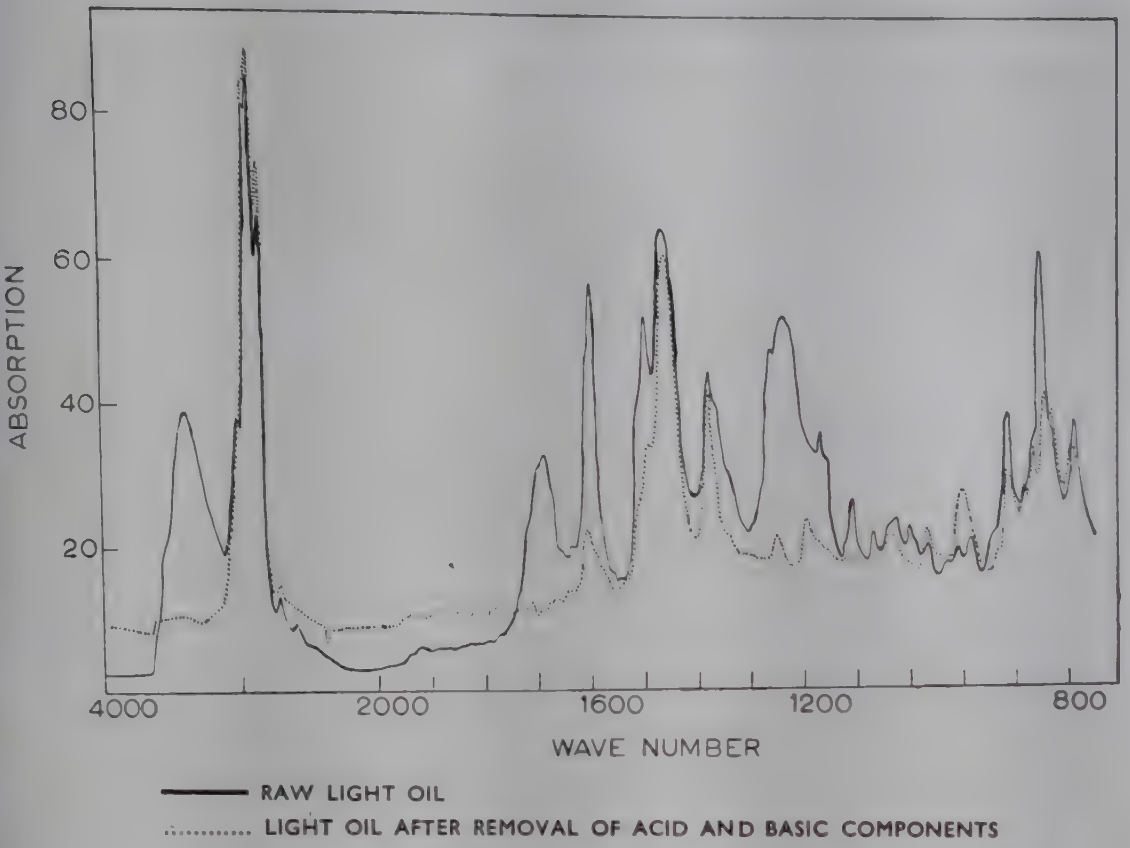

FIG. 1—INFRA-RED SPECTRA OF THE RAW AND PURIFIED LIGHT OIL NO. 64

The complete removal of acidic and basic components was controlled by comparison of infra-red absorption spectra of light oils before and after removal of these components. For instance, the broad band near 3400 cm.$^{-1}$ (hydrogen bonded O-H and N-H groups) which appeared in the spectrum of raw light oil No. 64 is absent in the spectrum of same after the removal of acidic and basic components (Fig. 1). It shows that the methods used for removal of acidic and basic compounds were sufficiently good.

The properties of neutral hydrocarbon portion of light oils are presented in Table 7.

The contents of various hydrocarbon groups were determined in this neutral portion. Olefins were estimated with 80 per cent sulphuric acid and from iodine numbers[4]. Aromatics were determined by three methods: (*a*) chromatography of fractions of light oils with silica gel as adsorbent[7], (*b*) from aniline points determined before and after removal of aromatics with the aid of 100 per cent sulphuric acid[5], and (*c*) from refractivity indexes determined before and after removal of aromatics[6]. Paraffins and naphthenes were calculated from difference. The results are presented in Table 8.

In general these results correspond to the results of Mrs Ihnatowicz[8] and of Jaeger and Kattwinkel[9] obtained with respect to light oil from bituminous coal.

TABLE 7—THE PHYSICOCHEMICAL PROPERTIES OF LIGHT OILS BEFORE AND AFTER REMOVAL OF NON-HYDROCARBON COMPONENTS

Sample No.	d_4^{20}	n_d^{20}	Viscosity (20°C.) in centipoises	Mol. wt	Iodine number	Aniline point °C.
45 before	0·8782	1·48019	1·3938	130	—	—
after	0·8313	1·46782	0·8796	137	103	10·3
64 before	0·8980	1·48634	1·4655	135	—	—
after	0·8433	1·47211	0·9358	143	117	10·8
65 before	0·8261	1·46295	0·7461	119	—	—
after	0·8042	1·45645	0·7264	125	98	16·7
89	0·7400	1·41923	0·6684	140	1·6	65·5

TABLE 8—THE COMPOSITION OF HYDROCARBON PART OF LIGHT OILS AND GASOLINE

Sample No.	Olefins %	Aromatics %	Paraffins and naphthenes %
45	24·7	54·1	21·2
64	27·7	52·4	19·9
65	21·9	51·6	26·5
89	0·4	6·2	93·4

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Benzole from Low Temperature Carbonization of Kothagudem Coal

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Benzole recovery by adsorption and wash-oil scrubbing methods from low temperature carbonization gases showed that 18-23 litres of benzole can be obtained from one ton of Kothagudem coal, the adsorption method giving higher yield and benzole of better quality. The benzole has a higher aromatic content consisting mostly of benzene, toluene and xylenes. n-Octane, n-decane, thiophene, pyridine and methyl ethyl ketone were also found to be present. By hydrofining the once-run benzole over a catalyst containing cobalt and molybdenum at 400 C., 30 kg./sq. cm. and a space velocity of 1, sulphur compounds were completely hydrogenated and only 87% of nitrogen bases were removed.

Benzole is recovered from carbonization gases by absorption in hydrocarbon wash-oils, adsorption on active carbons or cooling and condensation, of which the oil-washing process is the most generally employed with varying process conditions. The composition and amount of benzole produced in a plant vary with the carbonization conditions, the type of coal and method of recovery employed. The yield of light oil increases with the volatile content of the coal. The high temperature benzoles will be essentially aromatic in composition, while the low temperature benzoles contain more aliphatic, naphthenic and olefinic compounds with correspondingly smaller amounts of aromatics[1].

Benzole refining is mainly done by washing with concentrated sulphuric acid and catalytic hydrogenation under pressure. Hydro refining is a recent process developed for refining petroleum distillates and benzoles. There is no reduction in the content of aromatics and yields of 97-99 per cent are easily obtained. Since benzoles from low temperature carbonization (l.t.c.) contain larger amounts of olefins, hydrogenation seems to be the most suitable method of refining.

EXPERIMENTAL

Recovery. Benzole recovery from gases produced in the Lurgi-Spuelgas l.t.c. pilot plant from Kothagudem coal at 650°C., was carried out both by adsorption on active carbon and wash-oil counter-current scrubbing. The adsorption experiments were carried out in a 3 ft long and 1·5 in. i.d. mild steel column employing "Benzorbon", an activated carbon. The desorption of benzole from benzorbon was done with dry steam. The counter-current wash-oil scrubbing was carried out in a 3 ft long and 3 in. i.d. mild steel column packed with 0.25 in. ceramic raschig rings. It was provided with a perforated plate at the bottom and an oil spray at the top. L.t. tar distillate of B.P. 200-300°C. was used for absorption. The benzole was recovered by the distillation of benzolized wash-oil. About 4 litres of wash-oil was used for scrubbing and it was recirculated. Flow-sheets of the apparatus for both the methods are shown in Figs. 1 and 2.

Hydrorefining. The l.t. benzole was refined by hydrogenation over a catalyst containing oxides of cobalt and molybdenum. It was carried out in an apparatus consisting of a special steel reactor tube of 12 mm. i.d., 4 mm. wall thickness and 1 m. length. The flow sheet is given in Fig. 3.

Analysis. Crude l.t. benzole was distilled according to ASTM D-86 and the distillate up to 180°C. was taken as once-run benzole for subsequent analysis. The analysis of once-run and hydrorefined benzole was done by ASTM and STPTC methods. The hydrocarbon types in benzole were separated by adsorption chromatography on silica gel in a glass column of 7 ft length and 1 in. i.d. using a fluorescent dye (FIA). Fractional distillation was carried out in a Piros Glover Spinning Band Micro-Fractionation Column equivalent to 55 theoretical plates and at atmospheric pressure.

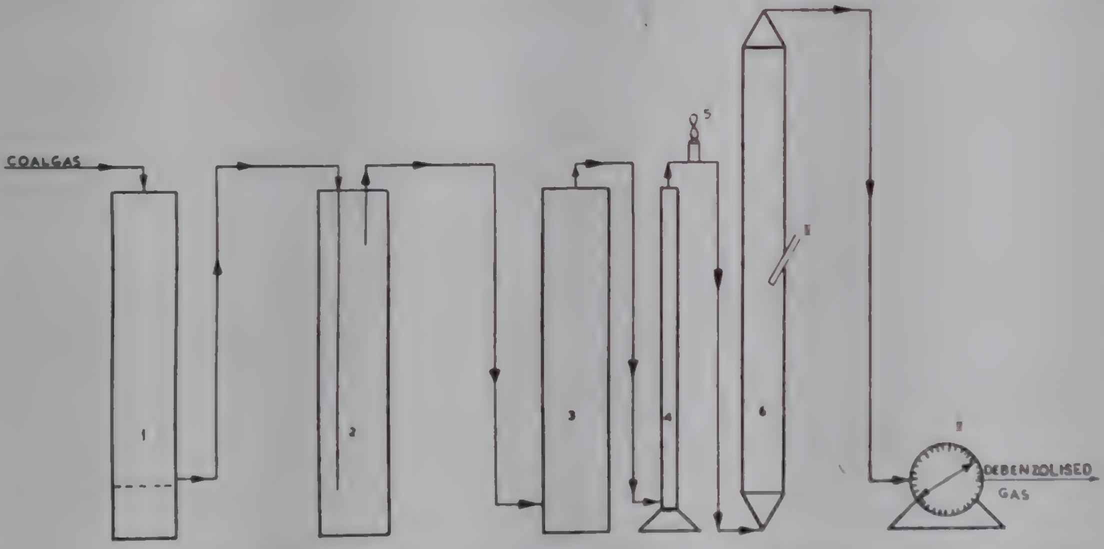

FIG. 1—FLOW-SHEET FOR THE RECOVERY OF LOW TEMPERATURE BENZOLE BY ACTIVE CARBON ADSORPTION: (1) Entrainment separator, (2) Container for ammoniacal cadmium chloride solution, (3) Entrainment separator, (4) Rotameter, (5) Thermometer, (6) Adsorber, and (7) Gas meter

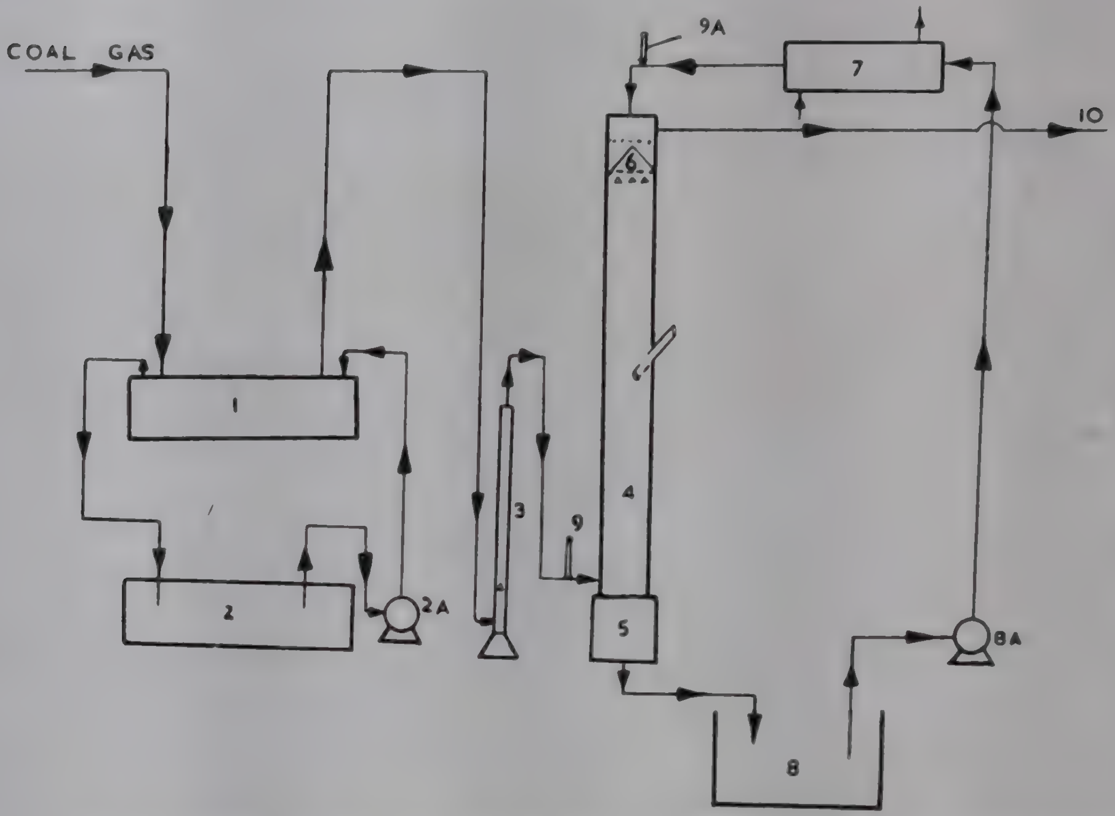

Fig. 2—Flow-sheet of the recovery of low temperature benzole by wash-oil scrubbing: (1) Gas cooler (Shell & Tube), (2) Water tank connected to refrigeration plant, (2A) Water pump, (3) Rotameter, (4) Scrubber, (5) Catch pot, (6) Spray, (7) Wash-oil cooler, (8) Wash-oil tank, (8A) Wash-oil pump, (9 & 9A) Thermometers, (10) Debenzolized gas to atmosphere

The gas chromatograms of the fractions were taken on a Griffin-George V.P.C. Mark II apparatus and the I.R. spectra on a Perkin-Elmer, Model 21, I.R. Spectrophotometer.

RESULTS AND DISCUSSION

The results shown in Tables 1 and 2 indicate that about 18-23 litres of l.t., benzole can be obtained from one ton of Kothagudem coal by employing efficient methods of recovery. The adsorption method gave a greater benzole yield of 21·3 litres per ton of coal as compared to 17·7 litres by wash-oil scrubbing. The efficiency of benzole recovery will be generally about 90-95 per cent by adsorption and 80-90 per cent by absorption in wash-oils. Benzorbon used in this investigation is a special grade of active carbon having very large surface area and high adsorptive capacity and hence benzole recovery was more efficient. Landa[2] had shown that the presence of higher molecular weight phenols and unsaturated hydrocarbons in the wash-oil reduces its absorption capacity. The usual molecular weight of wash-oils for benzole absorption is about 170 and if it rises to 200, the wash-oil has to be changed and replaced by fresh oil[3]. A wash-oil having

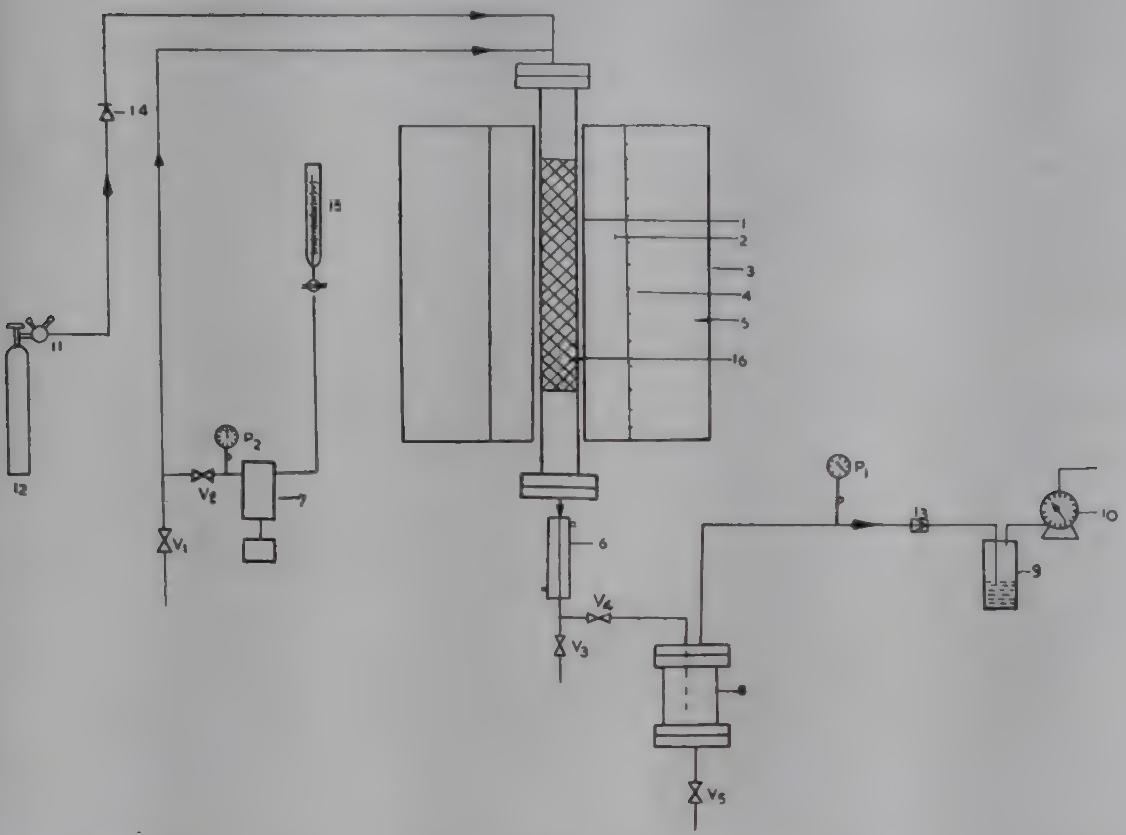

FIG. 3—FLOW-SHEET FOR HYDRO-REFINING OF LOW TEMPERATURE BENZOLE: (1) Reactor, (2) Steel block, (3) Sheet metal casing, (4) Heating coil, (5) Insulation, (6) Cooler, (7) Pump, (8) Separator, (9) Gas purifier, (10) Gas meter, (11) Pressure regulating valve, (12) Hydrogen cylinder, (13) Regulating valve, (14) Check valve, (15) Burette with feed, and (16) Catalyst

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TABLE 1—WASH-OIL PROPERTIES AND RESULTS OF BENZOLE RECOVERY BY COUNTER-CURRENT SCRUBBING

(Source of wash-oil: L.t. light tar from Kothagudem coal)

Properties of Wash-oil:

I.B.P., 200°C
50% boiling at 270°C.
90% boiling at 300°C.
Viscosity (Redwood No. 1) 46 sec.

Average M.W. (Cryoscopic) 187
Tar acids (% V/V) 20

Experimental Results:

Quantity of wash-oil taken	4 litres
Wash-oil rate	3·5 litres/min.
Gas rate	10 litres/min.
Temp. of scrubbing	24°C.
Crude benzole yield (up to 180°C.)	12·2 ml./Nm^3 of gas; 17·7 litres/ton of coal

TABLE 2—PROPERTIES OF BENZORBON AND RESULTS OF BENZOLE RECOVERY BY ADSORPTION

Size of benzorbon	Cylindrical pellets, 4 mm. long and 2·0 mm. diam.
Bulk density	400 Kg./Nm^3
Surface-area (B.E.T.)	1300 sq. m./g.
Quantity of benzorbon	350 g.
Temp. of adsorption	27°C.
Gas rate	2 litres/min.
Crude benzole yield up to 180°C.	14·7 ml./Nm^3 of gas; 21·3 litres/ton of coal

20 per cent of mainly high boiling tar-acids, about 15 per cent of unsaturated hydrocarbons and a molecular weight of 187 was used in this investigation and may be considered less efficient for benzole absorption. The lower benzole yield obtained by wash-oil scrubbing in this investigation may also be due to lesser efficiency of the scrubber. A lower scrubbing temperature 15-20°C. may increase the absorption efficiency.

The amount of benzole present in l.t.c. gases from Kothagudem coal is higher than the usual quantities recovered from coke-oven gases. The latter contain about 1 per cent by volume of benzole and the benzole yield will be about 13·6 litres per ton of coal, whereas 18-23 litres can be obtained from l.t.c.[4] During carbonization, the primary products formed are paraffinic which undergo a secondary decomposition in the hot zone of the charge. In l.t.c., the milder conditions prevailing in the carbonization chamber favour the preservation of the original primary paraffins and hence the actual quantity of benzole present in the gases is more but less aromatic. The length of carbonization period and the free-space above the charge may also influence the quantity and quality of benzole. Kothagudem coal with a high volatile content of 36 per cent (DMF) can be expected to give a high benzole yield.

The results of the analysis of once-run l.t. benzole are shown in Tables 3 and 4. There are no significant differences between the properties of benzole recovered by adsorption and absorption. Benzole obtained by adsorption on benzorbon is light yellow in colour with a lower specific gravity, whereas the one recovered by absorption is bright yellow with a higher specific gravity. The benzole from wash-oil scrubbing always contains some wash-oil constituents as carry-over during distillation. It is interesting to note that tar acids are not present in both types of benzoles and they contain almost equal amounts of tar bases and sulphur.

The hydrocarbon types present are almost the same in both the benzoles. L.t. benzole from Kothagudem coal contains about 47 per cent of aromatic

TABLE 3—PROPERTIES OF L.T. BENZOLE

PROPERTIES	METHOD OF RECOVERY	
	Wash-oil scrubbing	Adsorption on benzorbon
I.B.P., °C.	65	57
50% boiling at, °C.	131	130
Distillate up to 180°C., %	98·5	96
Sp. gr. at 15·5°C.	0·83	0·79
Colour (Lovibond Tintometer 1 in. Cell; Y+10R)	6·8	2·9
Hydrocarbon types (FIA) % V/V		
Saturates	20·5	20·8
Olefins	32·1	32·3
Aromatics	47·4	46·9
Naphthenes (aniline point and refractivity intercept methods)	nil	nil
Tar acids (STPTC)	Traces	Traces
Tar bases (STPTC), %	0·44	0·42
Sulphur (Bomb Calorimeter ASTM), %	0·73	0·7

TABLE 4—IMPORTANT CONSTITUENTS OF L. T. BENZOLE FROM KOTHAGUDEM COAL

COMPOUND	% V/V IN ONCE-RUN BENZOLE	METHODS OF IDENTIFICATION AND ESTIMATION
Benzene	5·4	Fractionation, gas chromatography and IR
Toluene	13·6	do
Ethylbenzene	2·4	do
m- and p-Xylenes	9·5	do
o-Xylene	3·9	do
n-Heptane	Identified but not estimated	Fractionation and gas chromatography
n-Octane	do	do
n-Nonane	do	do
n-Decane	do	do
Ethylmethyl ketone	do	Fractionation, gas chromatography and I.R.
Thiophene	do	do
Pyridine	do	do

hydrocarbons. Naphthenes are probably in very low concentration. It has been reported[5–8], that the light oils from l.t.c. contain about 25 per cent of saturates, 50 per cent of olefins and 25 per cent of aromatics. The saturated hydrocarbons consist of approximately 2/3 paraffins and 1/3 naphthenes. The higher aromatic and lower saturated and olefinic content of l.t. benzole from Kothagudem coal indicates that the primary products of carbonization may be undergoing a mild type of secondary decomposition in the carbonization chamber.

Some of the important constituents of l.t. benzole are presented in Table 4. All these compounds have already been reported to be present in benzoles.

Hydrorefining of l.t. benzole was carried out under different conditions of temperature, pressure and space-velocity. The analyses of the feed material and the refined product obtained at 400°C., 30 kg./sq. cm. pressure and 1·0 space-velocity are given in Tables 5 and 6. Results indicate that sulphur compounds are completely hydrogenated whereas only 88 per cent of tar bases are removed. The olefin hydrogenation was about 91 per cent. It has been reported that sulphur compounds will get hydrogenated easily than the nitrogen compounds[9]. The activation energies required for removal of sulphur and nitrogen compounds are about 3·8 and 20 k.cal./g. mole respectively. The results obtained are in accordance with this.

The reduction in specific gravity and refractive index and the increase in aniline point of the refined product are in good agreement with increase

TABLE 5—PROPERTIES OF CRUDE BENZOLE, USED FOR HYDROREFINING

I.B.P., °C.	76
50% boiling at, °C.	141
Distillate up to 180°C., %	96
Colour (Y+10R)	30·0
Sp. gr. at 15·5°C.	0·8250
n_d^{20}	1·4612
Aniline point	Below 0°C.
Total sulphur, %	0·6
Total nitrogen, %	0·18
Tar acids	Traces
Tar bases, %	0·4
Hydrocarbon types (FIA) (% V/V):	
Saturates	20·6
Olefins	27·7
Aromatics	51·7

TABLE 6—PROPERTIES OF REFINED BENZOLE

(Temp., 400°C.; pressure, 30 kg./sq. cm.; space-velocity, 1·0)

I.B.P., °C.	70
50% boiling at, °C.	139
Distillate up to 180°C., %	93
Colour (Y+10R)	2·0
Sp. gr. at 15·5°C.	0·803
n^{20}_{d}	1·4540
Aniline point, °C.	12·75
Total sulphur	nil
Total nitrogen, %	0·0021
Tar acids	nil
Tar bases, %	0·05
Hydrocarbon types (% V/V):	
Saturates	46·8
Olefins	2·5
Aromatics	50·6

in the saturates and decrease in the olefin content. The aromatic content of the feed and product remained almost same indicating that no significant hydrogenation of aromatics took place.

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Recovery of Benzole from L. T. C. of Some Indian Coals: A Comparative Study of Yields and Characteristics

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Results on the recovery of l.t. benzole from Kothagudem, Mandamari and Ghughus coals by active carbon adsorption show that 13-18 litres of benzole can be obtained per ton of coal. The benzole contains 44-47 per cent aromatics, 32-34 per cent olefins and 20-22 per cent saturates. Catalytic hydrogenation appears to be the best method for refining these benzoles. By hydro-dealkylation of these benzoles, substantial quantities of benzene can be economically produced.

One of the important methods of benzole recovery is by adsorption on active carbon, carried out in fixed beds. It is a batch process and is made continuous by employing several adsorbers. This method gives higher yields of better quality benzole without any contamination. Removal of hydrogen sulphide from gas prior to benzole recovery, maintenance of proper temperature during adsorption and desorption, are important in recovering benzole by this process. For effective removal of lighter constituents of benzole from gas, the adsorption must be stopped when the adsorbent is two-thirds saturated with benzole[1].

Many adsorbents have been investigated but only active carbon is found suitable for benzole recovery. Special types of active carbons have been developed to meet the particular conditions in benzole recovery. "Benzorbon" has been reported to be one of the best grades of active carbon available for this purpose[2].

Not much work appears to have been done on the recovery of l.t. benzoles and their characteristics. In view of the proposed establishment of several l.t.c. plants in India in the near future, an investigation on the recovery and general characteristics of l.t. benzole is important.

EXPERIMENT

Recovery. L.t. benzole was recovered from the gases evolved during carbonization of Kothagudem, Mandamari and Ghughus coals in a Lurgi-Spuelgas pilot plant at 650°C. by adsorption on "Benzorbon" in a 3 ft long and 1·5 in. i.d. mild steel column. In each experiment 350 g. of fresh benzorbon was used. The desorption was carried out with dry steam maintaining the temperature of the adsorbent at 100°C. by a heating tape. Hydrogen sulphide was removed by bubbling the gas through a cadmium chloride solution before it enters the adsorbent.

Analysis. Crude benzole was distilled according to ASTM D-86, and the distillate up to 180°C. was used for analysis by the ASTM and STPTC methods. The hydrocarbon types were determined by the Fluorescence Indicator Adsorption (FIA) method.

RESULTS AND DISCUSSION

The yields of crude l.t. benzole from Kothagudem, Mandamari and Ghughus coals, as shown in Table 1, are 17·7, 19·9 and 21·7 litres per ton respectively. The actual yields of benzole boiling up to 180°C. are 16·8, 18.6 and 20·8 litres respectively (Table 2). It is seen from Tables 3 and 4 that the benzole yield is related to the volatile matter and hydrogen content of the respective coals. The production of tar is also in the same order. This is in conformity with the already published data.

There are no significant differences in the properties of benzoles from these three coals (Table 2). They are light yellow in colour and possess a low specific gravity of about 0·8. The hydrocarbon type analysis shows that they are almost similar in composition with 20-22 per cent saturates, 32-34 per cent olefins and 44-47 per cent aromatics. The aromatic content is lower than in coke-oven benzoles but higher than in the normal l.t. benzoles reported in literature. The possible reasons for such a high aromatic content are discussed in an earlier communication[3]. The quantities of sulphur and nitrogenous bases present in l.t. benzoles are related to the

TABLE 1—YIELDS OF L.T. BENZOLE
(Temperature of adsorption, 27°C.)

COAL	GAS RATE (Nm³/min.)	TOTAL GAS PASSED (Nm³)	BENZOLE OBTAINED (ml./Nm³)	GAS/TON OF COAL (Nm³)	YIELD OF BENZOLE/ TON OF COAL (litres)
Kothagudem	0·005	3·045	12·2	1,450	17·7
Mandamari	0·005	3·045	16·0	1,360	19·9
Ghughus	0·005	3·045	13·5	1,460	21·7

TABLE 2—PROPERTIES OF L.T. BENZOLES

Source of coal	Kothagudem	Ghughus	Mandamari
Distillation Data:			
I.B.P., °C.	57	55	58
50% boiling at, °C.	130	115	115
Distillate up to 180°C., %	96	94	95
Colour (Lovibond Tintometer, 1 in. Cell, Y+10R)	2·9	..	..
Sp. gr. at 15·5°C.	0·79	0·79	0·79
Hydrocarbon Type (% V/V):			
Saturates	20·8	22·0	21·6
Olefins	32·3	34·0	33·3
Aromatics	46·9	44·0	45·1
Sulphur, wt %	0·7	0·85	0·81
Tar acids, vol. %	Traces	Traces	Traces
Tar bases, vol. %	0·42	0·15	0·15

TABLE 3—ANALYSIS OF COALS (% w/w)

Coal	Volatile matter (dry-basis)	Carbon (d.m.f.)	Hydrogen (d.m.f.)	Sulphur	Nitrogen
Kothagudem	28·1	80·7	4·3	0·36	1·25
Mandamari	31·6	80·0	4·9	0·70	1·17
Ghughus	34·1	84·1	5·1	0·60	

TABLE 4—YIELDS OF TAR AND BENZOLE (% w/w on coal basis) FROM LURGI-SPUELGAS PILOT PLANT AT 650°C.

Coal	Tar yields		Total tar yield	Benzole yield
	Light	Heavy		
Kothagudem	2·86	2·32	5·2	1·41
Mandamari	3·20	3·10	6·3	1·60
Ghughus	4·05	2·44	6·5	1·74

sulphur and nitrogen contents of respective coals. The benzoles contain tar bases but negligible tar acids.

Thus l.t. benzole produced in the Spuel-gas plant differs in composition not only from coke-oven benzole but also from normal l.t. benzoles reported.

Benzole is refined by washing with concentrated sulphuric acid by chlorination or by catalytic hydrogenation under pressure. The main drawback of the acid refining process is the loss amounting to 10-15 per cent of feed since sulphuric acid removes all the olefinic hydrocarbons. Further, the disposal of the acid tar is difficult and costly. The chlorination process also has similar drawbacks. Since the l.t. benzole from some of the coals reported here contains higher percentage (30-35 per cent) of olefins, losses on acid refining or chlorination will be more. On the other hand, in the hydrorefining process, the yield is about 98-99 per cent, as the olefinic hydrocarbons are converted to saturates and are retained in the product. No undesirable byproduct is formed. Hence catalytic hydrorefining appears to be the most advantageous method of refining l.t. benzoles of this type. If central refining plants of large capacities are established, the process will be quite economical.

There are two main outlets for benzole: (i) production of motor benzole; (ii) extraction of benzene, toluene, etc. for chemical industry. L.t. benzole with about 50 per cent of aromatics will have a high octane value and can be used as a high antiknock motor fuel after refining. But it cannot be a direct source of benzene like coke-oven benzole. Since it contains about 50 per cent of benzene and alkylbenzenes, it has to be subjected to hydro-dealkylation for the production of benzene and gas of high calorific value. One ton of coal yields about 18-23 litres of l.t. benzole which in turn may be dealkylated to produce about 6·5 litres of benzene. Hence hydro-dealkylation can be an important method to process l.t. benzoles for economic production of benzene.

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The author wishes to express his thanks to Dr S. Husain Zaheer and Dr M. G. Krishna, for valuable guidance and help in carrying out the work. Thanks are also due to Dr R. Vaidyeswaran and other colleagues of the Coal Division for valuable help.

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Use of Benzole Meter in the Estimation of Benzole Content of Low Temperature Carbonization Gases

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The factors affecting the efficiency of benzole recovery are mentioned. The importance of accurate measurement of benzole in rich and lean gas for efficient recovery of benzole is stressed. Methods of measuring benzole content in carbonization gases are described. Results obtained on the estimation of benzole present in the l.t.c. gases from Kothagudem coal using the "Hanovia Benzole Meter" are presented.

Benzole is an important byproduct of coal carbonization and can be recovered in all types of carbonization plants whenever economically feasible. Coke-oven benzole forms one of the main sources of aromatic hydrocarbons. In view of the growing competition from petroleum industry, efforts have to be made to maintain high efficiency in benzole recovery to make the process more economical. The efficiency mainly depends upon the methods of recovery, for which accurate measurement of benzole in rich and lean gas is necessary. Work had already been done on the methods of recovery, but it is only in recent times that attention has been paid on the methods for accurate measurement of benzole in coal gas. Different types of instruments have been developed for intermittent or continuous measurement of benzole in gas by the techniques of gas liquid chromatography and spectrophotometry.

The general practice in benzole recovery plants is to burn a small quantity of the lean gas continuously in a test flame and a sudden increase in the luminosity of the flame is taken as an indication of the 'slip' of benzole.

This is a very rough method and does not give any indication of the amount of benzole escaping in the lean gas. Although maintenance of a constant 'slip' of benzole in the lean gas gives a fair indication of the working of the plant, it alone is not sufficient, since the benzole content of the lean gas changes with that of the rich gas. Hence a correct measurement of the benzole present in both the rich and lean gases is essential for measuring the efficiency of the plant so that the recovery conditions may be maintained constant and at maximum level.

Efficiency of benzole recovery is usually determined with respect to a low boiling constituent of benzole, usually benzene, since it is the most valuable and low boiling constituent of benzole. If the recovery of benzene is complete, the other higher boiling compounds may also be expected to have been satisfactorily recovered.

St. Claire-Deville method is the classical one used for measuring the efficiency of benzole recovery by first condensing the volatile constituents of coal gas at −80°C. in sufficient quantity and then determining the amount of benzene or any other constituent present by regular analysis. This method is both time-consuming and laborious and hence not much used. With the advent of the gas liquid chromatographic techniques and instruments, it has become possible to measure the efficiency of benzole recovery with respect to any one of its constituents accurately and quickly. This can be done only on an intermittent basis at regular intervals. A more accurate and elegant method is to introduce small samples of rich and lean gas at regular intervals by automatic sampling valves into a gas liquid chromatographic apparatus to which an analogue computer is attached. This type of instrument can record the ratio of the concentration of any benzole constituent in rich and lean gas[1]. Such an instrument is reported to be under development by the National Benzole Company.

Continuous measurement of benzole in the coal gas will give a better picture of the changes taking place in both the carbonization and benzole recovery plants. It is now possible to record the benzole content of the rich and lean gas continuously by the use of photometric instruments like the "Hanovia Benzole Meter". It consists of a sensitive photometer in which the gas cell is interposed between a low-pressure mercury lamp and a photo-electric detector. Ultraviolet light of 2537 Å emitted by the discharge tube is passed through the gas chamber and depending upon the concentration of benzole in the gas causes photo-current to be developed by the photo-electric tube. Benzene, toluene and xylenes give selective and identical absorption of U.V. light at 2537 Å. Hence the benzole meter records the actual content of the BTX mixture present in coal gas. The instrument is capable of measuring up to 0·1 to 0·6 g. of benzole per 100 litres of coal gas. It will also respond in varying degrees to other important vapours with high absorption in the U.V. region around 2537 Å such as trichloroethylene, methyl-ethyl ketone, styrene, etc.

TABLE 1—BENZOLE CONTENT OF L.T.C. GASES

BTX content of l.t.c. gas from Kothagudem coal (according to benzole meter reading)	6 ml./Nm³
BTX content of l.t. benzole from Kothagudem coal (as determined by chromatographic and spectrophotometric methods)	33% V/V
Total benzole content of l.t.c. gas (from the above data)	18 ml./Nm³
Maximum l.t benzole yield from Kothagudem coal (obtained by active carbon absorption)	15 ml./Nm³

Coke-oven benzole contains about 95-98 per cent of benzene, toluene and xylenes and hence the benzole meter can be used to record almost the total quantity of benzole present in coke-oven gases. The l.t. benzole is less aromatic in nature and contains larger amounts of saturates and olefins which do not have absorption in the U.V. region around 2537 Å. From the benzole meter reading giving the measure of BTX content in coal gas and an accurate analysis of l.t. benzoles for benzene, toluene and xylenes content by other methods, the actual benzole content of l.t.c. gases can be calculated.

The "Hanovia Benzole Meter" has been successfully used to record the benzole content of the l.t.c. gases from Kothagudem coal produced in the Lurgi-Spuelgas l.t.c. pilot plant operating at the Regional Research Laboratory, Hyderabad. The results are shown in Table 1.

It is seen from Table 1 that the benzole meter indicates a higher value for the benzole content, which may be due to the following reasons:

1. In the experiments for benzole recovery by active carbon absorption, benzole might not have been removed completely.

2. There might have been losses during desorption of benzole from active carbon, distillation, fractionation in the spinning band column and separation of hydrocarbon types on chromatographic columns employed in the analysis.

3. Due to the presence of ethyl-methyl ketone (identified in l.t. benzole from Kothagudem coal) and probably other substances (unidentified) which may give absorption at 2537 Å, the benzole meter may have given slightly higher values.

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Changes in the Properties of Low Temperature Tar on Storage

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Studies on the changes in physico-chemical properties of low temperature tar showed that on storage viscosity, pitch yield, toluene insolubles and softening point of pitch increased. Sedimentation appeared to take place as evidenced by decrease in per cent transmission of light through tar spots on filter paper and also by flow rate measurements. Photomicrographs of fresh and stored tar samples showed segregation of particles on storage. Tar acids and some constituents of unsaturated hydrocarbons appear to have contributed to the decrease in flow rates.

Low temperature (l.t.) tar is different from high temperature tar in its chemical nature, behaviour on storage and thermal stability. L.t. tars being of primary type undergo substantial changes due to thermal decomposition and oxidation—polymerization during distillation[1]. Unsaturated molecules and some of the high molecular weight resinols are more susceptible than others. Also l.t. tars undergo alteration on storage and the extent of the alteration depends on the presence of air, light or heat[2].

Earlier workers found that freshly produced primary tars which are light yellow materials darken on exposure to air and light[3–6]. The darkening effect of the tar-distillate has been explained by Edwards[7] to be due to oxidation of a leuco compound of a condensed phenol. Jaegar[8] suggested that darkening of primary tar distillates was caused by air oxidation and to some extent by light and tar bases. Fisher and Ehrhardt[9] studied the action of air at 150°C. and 40 atmospheres pressure on tar and tar fractions. They concluded that phenols are changed to resins and implied that acid and hydrocarbons are attacked. Vahrman[1] suggested that many constituents of l.t. tars which are susceptible to oxidation may be precursors to polymerization reactions. According to him the better known of such reactions are those occurring in polyhydric phenols, unsaturated hydrocarbons and hydronaphthalenes.

During investigations conducted at this Laboratory on the utilization of l.t. tar fractions, samples taken from the main storage tanks after different periods exhibited different viscosities and distillation characteristics. In view of the influence of these changes on the handling and processing of tar, the present studies were undertaken to assess the variation in different properties of l.t. tar during storage.

MATERIALS

Tar obtained by low temperature carbonization of Kothagudem coal at 650°C. in a 25 tons/day capacity Lurgi-Spuelgas pilot plant operating at Regional Research Laboratory, Hyderabad, was used. The tar is condensed into two fractions—the heavy and light tars. The properties are given in Table 1.

TABLE 1—TYPICAL PROPERTIES OF HEAVY AND LIGHT TAR

Properties	Heavy tar	Light tar
Sp. gr. (25°C./25°C.)	1·07	0·98
Viscosity	41·9 secs. at 35°C. by B.R.T.A. 10 mm. cup viscometer E.V.T. = 33·9	55 secs. at 100°F. by Redwood No. 1 viscometer
Softening point, °C. (R and B)	28·0	..
Insoluble matter in toluene, %	1·01	0·8
Water content, vol. %	0·4	1·5
Distillation data, % by wt		
Initial boiling point, °C.	228	95
Up to 170°C.	..	1·5
170-210°C.	..	16·0
210-230°C.	0·63	19·0
230-270°C.	2·9	23·0
270-300°C.	7·81	13·5
300-360°C.	15·6	12·75
Residue at 360°C.	72·2	13·25
Tar acids in fraction up to 360°C., vol. %	30·0	28·0

NOTE: The properties of heavy and light tar depend upon the nature of coal and the carbonization conditions. A typical analysis is given in Table 1

EXPERIMENTAL PROCEDURE

The following four aspects on changes induced in l.t. tar on storage were studied:

General Physicochemical Properties of Tars. The heavy and light tar fractions were collected in 2 lb. capacity wide-mouth glass bottles as the tar was flowing into the tanks and stored under air. The fresh samples and samples after 15, 31, 61, 165 and 210 days of storage were analysed for sp. gr., toluene insoluble matter, distillation range and tar acid content in the distillate up to 360°C. Each time before the sample was taken for analysis the container was warmed to about 50-60°C. in an air-oven and the material was stirred well to ensure uniformity of the sample. The methods of analysis of the tar were as specified by the "Standardization of Tar Products Tests Committee", England.

Spot Tests of Tars. The "Oil Spot" test[10] is used in industrial practice for engine lubricating oil control. The spot test technique is adopted for the tars to get some correlation between fresh and stored tar samples by measuring percentage transmission of light through tar spots. A unit has been fabricated for this purpose which contains a source of light, condensing lens, a photocell and a galvanometer. Two drops of the tar sample are taken on a Whatman No. 1 filter paper. Galvanometer is first adjusted for 100 per cent deflection with reference to filter paper and then the test sample is introduced in between the source of light and the photocell. The deflection in the galvanometer is taken as per cent transmission.

Photomicrographs of Tars. Photomicrographs of smears of l.t. tar samples were taken using Leitz phase contrast microscope (magnification 200).

Flow Studies of Tar Oils. Even after so much advancement the petroleum industry is still facing difficulties in pumping and maintenance of continuous flow conditions[11]. Flow studies with different tar oils were made using a glass apparatus shown in Fig. 1. Keeping a constant liquid head in the apparatus the quantity of liquid flowing through a stop cock 'A' in 5 min. was noted at regular intervals of ½ hr.

RESULTS AND DISCUSSION

General Physicochemical Properties of L.T. Tars. It may be observed from the results in Table 2 that:

- *(i)* the specific gravity and moisture content of the samples remained practically constant during storage;
- *(ii)* Toluene insoluble increased from 1 to 1·41 in heavy tar during seven months storage;
- *(iii)* the decomposition point decreased by about 13°C. for heavy tar and by about 10°C. for light tar. The pitch yield at

TABLE 2—EFFECT OF STORAGE ON THE PROPERTIES OF L.T. TAR

Properties	Fresh tar	Storage period, days				
		15	31	61	165	210
Heavy Tar:						
1. Sp. gr. (25°C./25°C.)	1·072	..	..	..	..	1·071
2. Toluene-insoluble matter, wt %	1·0	..	..	..	..	1·41
3. Moisture content, vol. %	0·4	0·43	0·43	0·42	0·42	0·44
4. Viscosity, E.V.T.	33·9	..	34·4	..	35·7	35·9
5. Softening point (R & B), °C.	28·0	..	29·0	..	31·5	32·0
6. Decomposition point, °C.	333	..	..	..	..	320
7. Analysis of the distillate (% vol.)						
up to 230°C.	0·63	0·66	0·65	0·63	0·62	0·63
230-270°C.	2·9	2·93	2·88	2·13	1·88	1·5
270-300°C.	7·81	7·04	5·5	4·3	3·8	3·6
300-360°C.	15·6	17·3	19·7	24·2	27·8	28·6
Residue at 360°C.	72·2	71·3	70·1	68·1	65·5	65·4
8. Tar acid in fraction 0-360 (% vol.)	29·00	..	..	..	..	32·0
Light Tar:						
1. Sp. gr. (25°C./25°C.)	0·979	..	..	..	..	0·98
2. Toluene-insolube matter	0·299	..	..	..	..	0·3
3. Moisture content, vol. %	1·1	1·01	1·2	1·3	1·3	1·5
4. Viscosity by Redwood No. 1 in secs.	43·5	..	..	..	54·0	56·0
5. Analysis of the distillate (% vol.)						
up to 170°C.	1·5	1·6	1·3	1·5	1·6	1·7
170-210°C.	16·0	14·5	13·4	12·4	10·5	10·0
210-230°C.	19·0	19·6	19·8	20·0	20·0	20·0
230-270°C.	23·0	24·2	25·5	26·4	25·8	26·0
270-300°C.	13·5	12·5	12·3	12·0	12·6	13·0
300-360°C.	12·75	12·6	12·1	11·5	12·8	12·5
Residue at 360°C.	13·25	13·8	14·1	15·0	16·0	16·3
6. Tar acids in fraction 0-360°C. (% vol.)	28·0	..	..	..	..	30·0
7. Decomposition point, °C.	315	..	..	..	..	305

NOTE: Samples of heavy and light tars, collected at different intervals and analysed after 1, 2 and 3 months storage have shown that there is no appreciable change in the properties such as sp. gr., toluene insoluble matter and tar acid content.

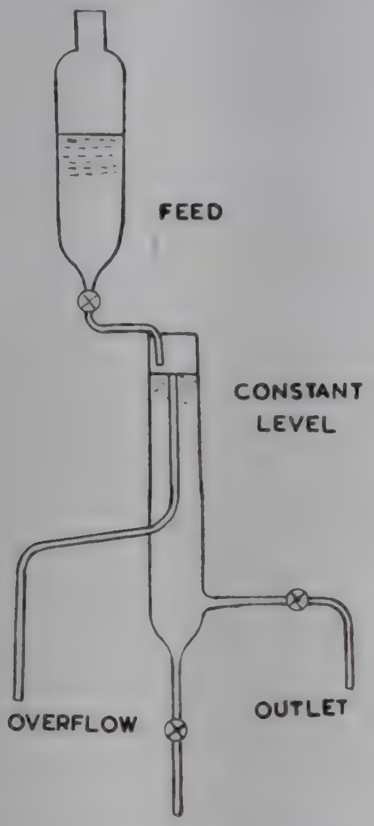

FIG. 1—APPARATUS FOR FLOW STUDIES

decomposition point increased from 80 to 87 per cent in heavy tar over the period of storage;

(*iv*) the viscosity (E.V.T.) increased from 33·9 to 35·9 for heavy tar and from 43·5 sec. to 56·0 sec. (Redwood No. 1) for light tar.

The above observations (*i*, *ii*, *iii*) are generally in conformity with the findings of Gomez and coworkers[2] who investigated the changes in properties of l.t. lignite tar on storage for 7 months. Green and Thakur[4] in their detailed studies on vertical retort tar reported about the increase in insoluble matter on storage. Parr and Olin[12] have also reported increase in viscosity of l.t. tar on storage and attributed it to atmospheric oxidation.

It is seen from Fig. 2 that fraction up to 230°C. remained constant, fractions 230-270°C. and 270-300°C. decreased by 1·4 and 4·2 per cent respectively, whereas fraction 300-360°C. increased by 12·3 per cent. Residue above 360°C. decreased by 6·1 per cent over the period of storage.

Similarly Fig. 2A shows that fraction up to 170°C. remained constant, and no appreciable change is noticed in the fractions 210-230°C., 270-300°C. and 300-360°C. Fraction 170-210°C. decreased by 6 per cent, whereas fraction 230-270°C. increased by 3 per cent. The residue at 360°C. also increased by about 3 per cent over the period of storage.

Spot Tests of Tars. The results in Table 3 and Fig. 4 indicate that as the light tar is stored for a longer period, the per cent transmission decreased. This may be due to sediment formation on storage. Similar studies with distillate fractions from fresh light tar and stored light tar showed a different trend. Fractions from stored light tar were found to give more transmission than fractions from fresh tar. From this it can be said that the colour forming bodies are retained in the pitch on storage.

TABLE 3—SPOT TEST OF TARS

Period of storage	% Transmission of light, after		
	2 hr	1 week	4 weeks
Fresh light tar	122·0	45	37·5
17 days	94	32·0	25·5
23 days	84	27·5	22·5
33 days	74	24·5	15·0
196 days	30·5	14·0	11·5
730 days	26·5	11·5	. .
2615 days	24·0	9·0	9·0

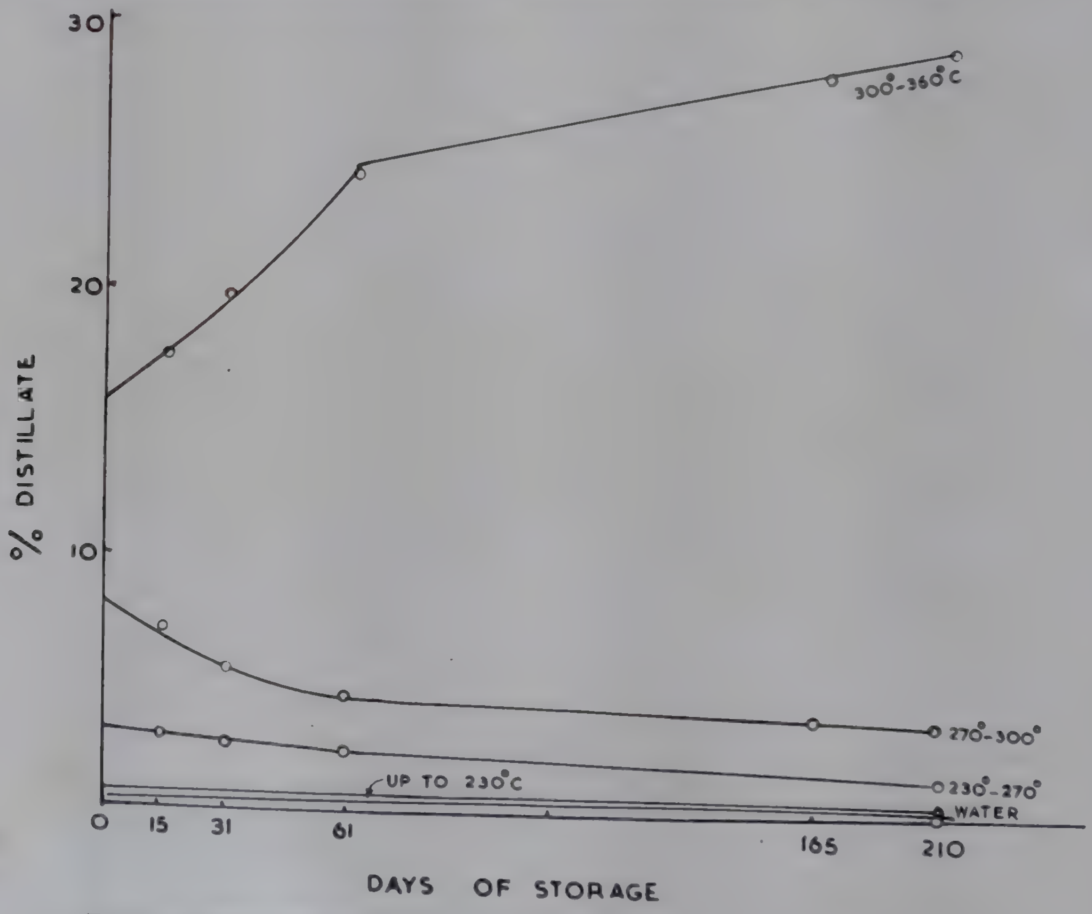

Fig. 2—Effect of storage on distillation characteristics of heavy tar

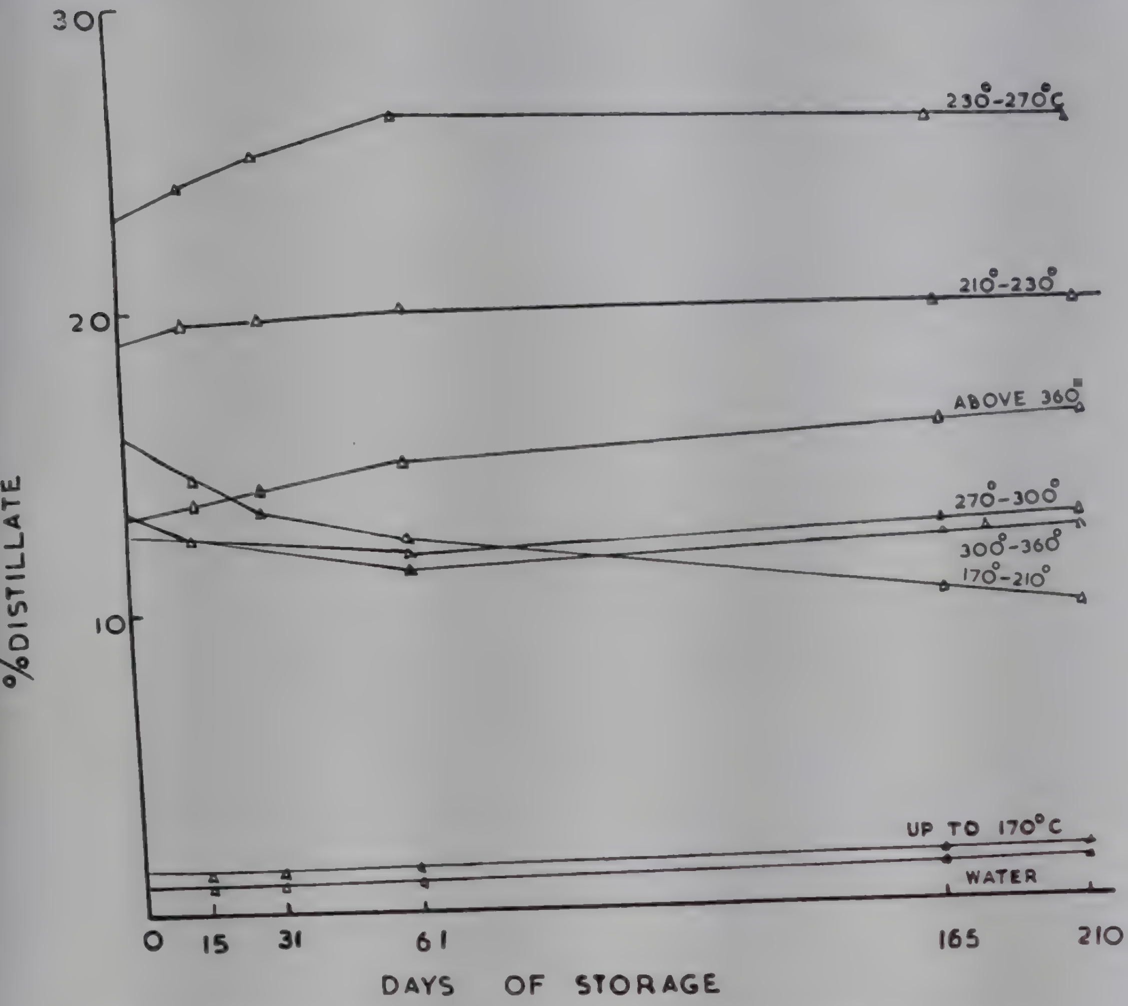

Fig. 2A—Effect of storage on distillation characteristics of light tar

Photomicrographs of Tars. It is generally accepted that tar is a colloid[13,14]. The size and shape of the "Micelles" of various tars was studied by means of electron microscope by Sarkar[15].

The photomicrographs giving the physical structures of l.t. tar, fresh and stored for one and six months are presented in Fig. 3(A-C). Unlike the fresh sample the stored samples showed segregation of particles which may be due to molecular growth on aging[2].

Nellensteyn[16] considers that tar is a sol-type dispersion of the more infusible resins as units of colloidal dimension in a continuous oily medium. A section of sandow (lignite) tar smear shows the presence of two liquid (oil and water) system, the oil system containing insoluble amorphous particles[17]. Smear of Delcarbon bituminous tar is composed of amorphous solid plates dispersed in an oily medium. Kothagudem tar smear stored for one month is composed of insoluble amorphous particles and amorphous solid plates dispersed in an oily medium. This indicates that Kothagudem tar is intermediate between tars from lignite and bituminous coals.

Flow Studies of Tar Oils. It is seen from Fig. 5 that the flow rate of fresh, filtered, light tar dropped to 50 per cent of original in 1 hr and to

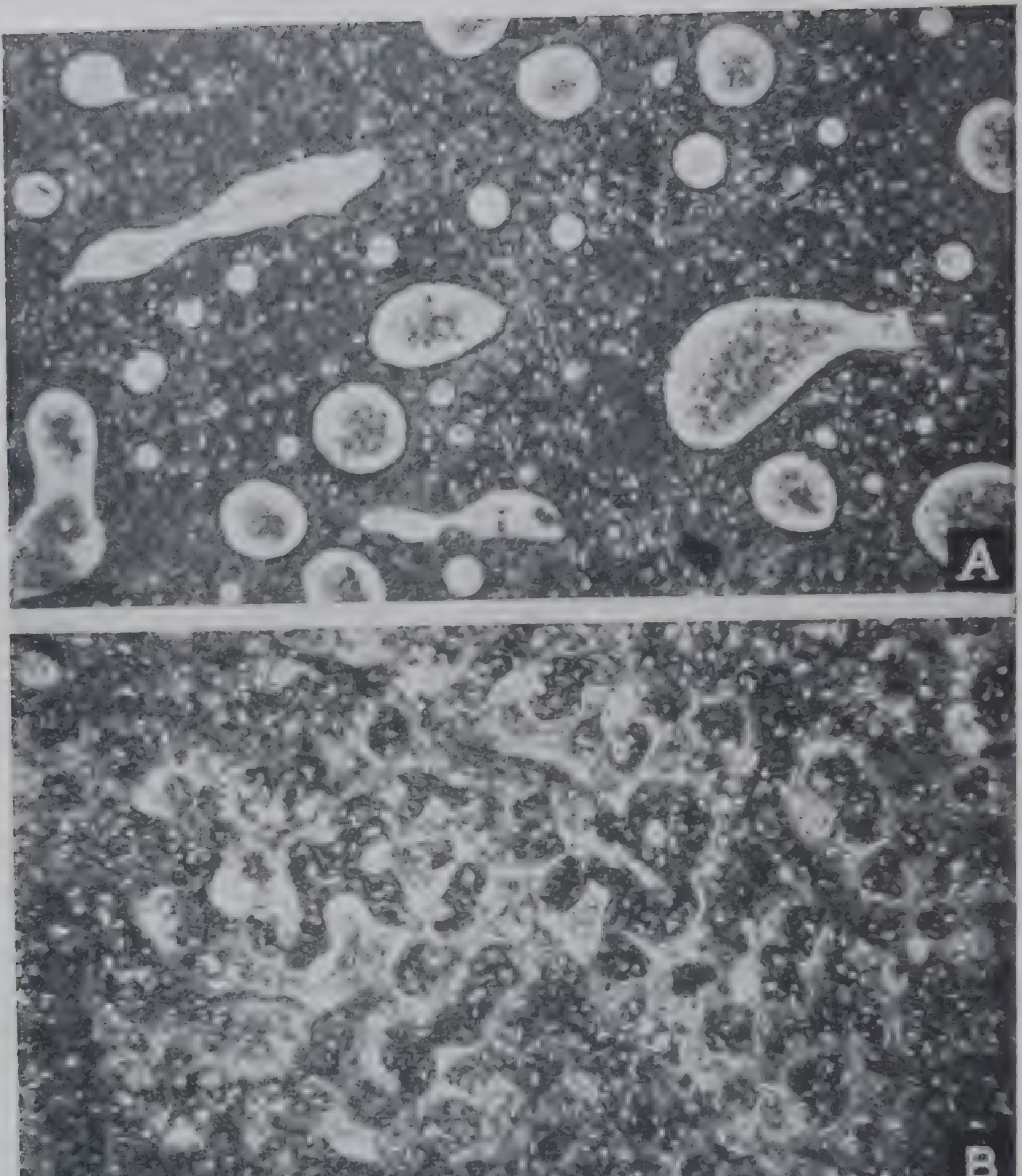

Fig 3(A-C)—A—Heavy tar—fresh; B—Heavy tar—stored for one month; C—Heavy tar—stored for six months

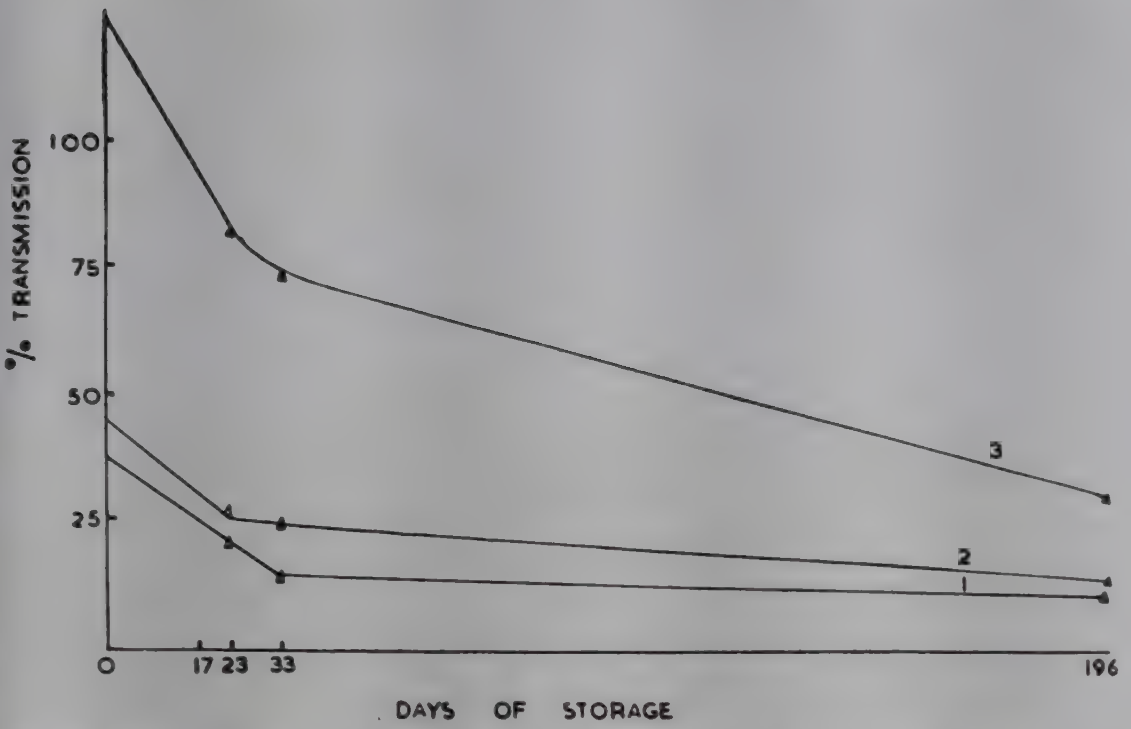

Fig. 4—Effect of storage on light tar (% transmission of light through spots of light tar). storage period: (1) 4 weeks, (2) 1 week, (3) 2 hr

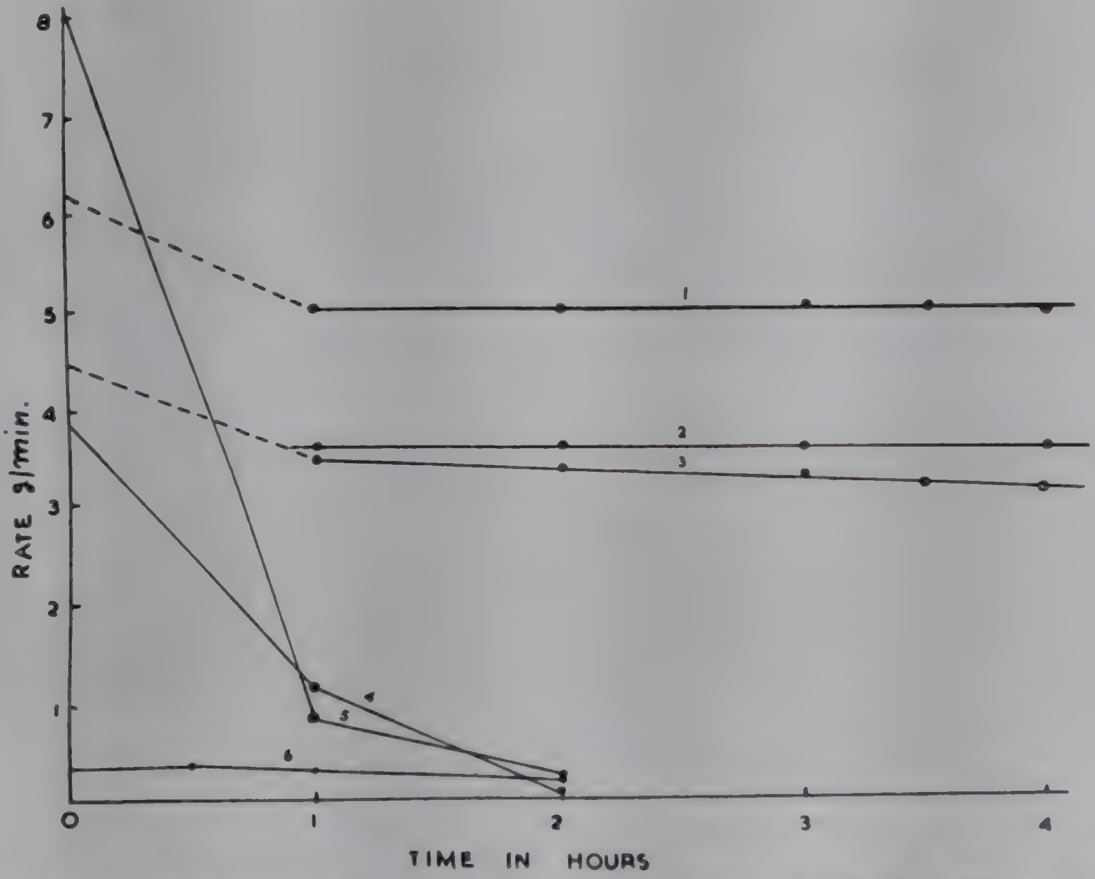

Fig. 5—Effect of storage on flow properties of tar oils: (1) Neutral oil from light tar (fresh), (2) Neutral oil from fraction up to 230°C. of light tar, (3) Neutral oil from stored light tar, (4) Stored light tar, (5) Fresh light tar, (6) Fraction up to 230°C.

TABLE 4—FLOW PROPERTIES OF TAR OILS

(Rate, g./min.)

TIME IN HOURS	LIGHT TAR FRESH	LIGHT TAR STORED	DISTILLED WATER	NEUTRAL OIL FROM			FRACTION BOILING UP TO 230°C.	ADDITION OF TAR ACID TO NEUTRAL OIL FROM 230°C. FRACTION			
				Light tar fresh	Light tar stored	Fraction boiling upto 230°C.		5%*	5%**	10%**	20%**
0 hr	16·64	8·176	3·0	6·176	4·45	3·65	0·336	4·252	6·79	3·98	2·568
0·5 hr	..	..	3·02	..	..	..	0·34	2·536	6·62	3·31	0·858
1 hr	8·514	0·84	3·03	5·01	3·47	3·60	0·266	2·45	6·45	3·25	0·474
1·5 hr	..	..	3·02	4·92	..	..	0·259	2·42	6·32	..	0·33
2 hr	1·604	0·252	..	5·001	3·364	3·62	0·249	2·416	6·22	3·22	0·242
2·5 hr	..	..	..	4·88	..	..	..	2·374	6·18	3·18	..
3 hr	0·398	..	..	5·092	3·32	3·62	..	2·367	6·09	3·09	..
3·5 hr	..	..	..	5·06	..	..	..	2·362	6·06	..	..
4 hr	..	..	..	5·02	3·13	..	..	..	..	..	..
4·5 hr	..	..	..	5·06	..	..	..	..	..	..	..

*Tar acid extracted from l.t. tar.

**Tar acid fractions (F_1 & F_2) obtained from tar acid fractionation plant.

about 3 per cent in 3 hr. In case of stored light tar the drop was about 90 per cent in 1 hr. The flow rates of filtered neutral oil samples prepared from (*i*) distillate fraction up to 230°C. and (*ii*) fresh light tar, remain reasonably constant over 4 hr. But in case of neutral oil from stored light tar the flow decreased.

When 5 per cent dehydrated tar acid was added to neutral oil from fraction up to 230°C., a black pitchy mass separated out and did not dissolve even on heating to 50°C.

Tar acid fractions F_1 (cresols—up to 205°C.) and F_2 (xylenols –205-230°C.) obtained from tar acid fractionation plant were re-mixed in the same proportions as found in the distillates and added to neutral oil from fraction up to 230°C. in 5, 10 and 20 per cent.

Table 4 indicates that flow rates decreased with higher tar acid contents. It is probable that tar acids are getting polymerized and causing reduction in flow rates.

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Distillation and Treatment of Low Temperature Tars under Pressure

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Studies on pressure distillation and pressure treatment of low temperature tars are reported. Specific gravity, boiling range and aromatic hydrocarbon content of the distillate fractions decreased and saturated hydrocarbons increased as the distillation pressures were increased up to 200 lb./sq. in. The softening point of residue increased. During the distillation of light tar (90 per cent boiling between 160-360°C.) under pressure, a marked decrease in specific gravity and boiling range of the distillates was noticed after the low boiling oils were removed. Heavy tar was found to be more susceptible to distillation under pressure than light tar. When heavy tar is heated under pressure, the changes in properties are not significant. The amount of noncondensable gases increases with the duration of the treatment.

An important byproduct of low temperature carbonization (l.t.c.) is the low temperature (l.t.) tar. It is considered to be a primary tar because it is obtained at relatively lower temperatures of carbonization (450-700°C.) without secondary pyrolysis at higher temperatures unlike high temperature (h.t.) tar. The chemical nature, properties and also behaviour of l.t. tar during storage, thermal treatment and distillation are considerably different from those of h.t. tar[1]. It is well known that the composition of tar changes with the type of coal, method of carbonization and the temperature of carbonization. Various workers[2-6] have reported the effect of distilling tar under pressure but most of the work pertains to h.t. tar or brown-coal tar. The present investigation was undertaken to study the variation in yields and composition of distillates during the pressure distillation and treatment of tars obtained from the l.t.c. pilot plant operating at the Regional Research Laboratory, Hyderabad.

MATERIALS AND METHODS

The l.t. tar used in these studies was obtained during carbonization at 650°C. of a non-caking coal from Kothagudem (Andhra) by the Lurgi-Spuelgas internal heating process. In the pilot plant, tar is condensed into two fractions, called light and heavy tar. Studies were carried out on these two tar fractions.

The distillates were tested for their boiling range, specific gravity and alkali-solubles by the STPTC methods[7] and for the Hydrocarbon types by FIA method[8]. Residues from heavy tar distillations were analysed for softening points by STPTC methods. Water contents of the samples were determined by Dean and Stark method[7].

APPARATUS

A laboratory stainless steel-clad mild steel still (Fig. 1) was used for the distillations and treatment under pressure. The main apparatus consisted of a still (1·8 litre capacity), fitted with a stainless steel needle valve, pressure gauge, safety valve and thermometer pockets. The condensing system consisted of an air condenser and a water cooled glass coil condenser. The still was heated by means of a cylindrical electric heater with a Sunvic regulator.

EXPERIMENTAL

Dehydration. The still was charged with 1 litre of the wet sample and assembled. Heating of the still was then begun and so regulated that pressure built up to about 25 lb./sq. in. in 40-50 min. Dehydration was then carried out by regulating both the heater and needle valve.

Pressure Distillation. After dehydration the needle valve was closed until the desired pressure developed in the still (about 5-15 min.) and then slowly opened. The needle valve and heater were regulated so as to maintain a distillation rate of 10-12 cc./min. Liquid and vapour temperatures were noted for every 50 cc. distillate and each 100 cc. fraction was separately collected. Heavy tar was distilled up to a distillate yield of 30 per cent and light tar to 70 per cent.

Pressure Treatment. Pressure treatment was done by heating the tar sample in the still, keeping the needle valve closed. After the still reached the desired pressure the heater was regulated to keep the pressure constant for the desired time. Vapour and liquid temperatures were noted every half-hour.

RESULTS AND DISCUSSION

Figs. 2-5 show the variation of the yields of distillate with liquid and vapour temperatures during distillation of the tar samples at pressures

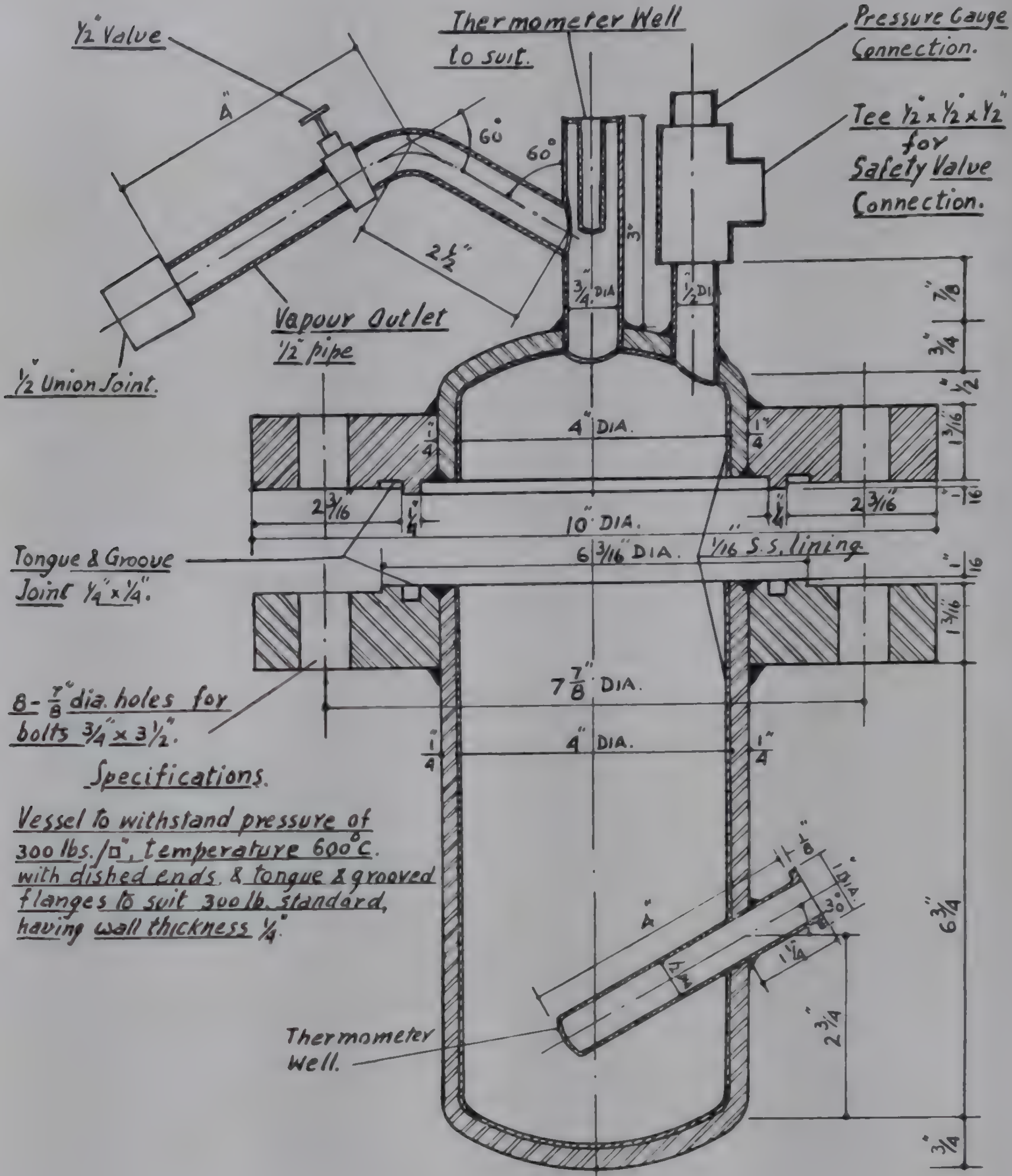
½" Valve
"A"
60°
60°
Thermometer Well to suit.
Pressure Gauge Connection.
Tee ½" x ½" x ½" for Safety Valve Connection.
3"
2½"
¾" DIA
½" DIA
Vapour Outlet ½" pipe
½" Union Joint.
7/8"
¾"
½"
4" DIA.
¼"
¼"
1 3/16"
1/16"
2 3/16"
2 3/16"
¼"
¼"
10" DIA.
6 3/16" DIA.
1/16" S.S. lining
Tongue & Groove Joint ¼" x ¼".
1/16"
1 3/16"
7 7/8" DIA.
8 - 7/8" dia. holes for bolts ¾" x 3½".
4" DIA.
¼"
¼"
Specifications.
Vessel to withstand pressure of 300 lbs./□", temperature 600°C. with dished ends. & tongue & grooved flanges to suit 300 lb. standard, having wall thickness ¼".
"A"
1/8"
1" DIA.
30°
1¼"
¼"
2¾"
6¾"
Thermometer Well.
¾"

FIG. 1—DISTILLATION STILL

ranging from atmospheric to 200 p.s.i.g. Boiling ranges of these distillates are shown in Figs. 6 and 7. A plot of temperature vs pressure during pressure treatment is shown in Fig. 8.

Tables 1 and 2 give data on yields, specific gravities, alkali solubles and hydrocarbon types of distillate fractions. Table 3 gives the effect of duration of pressure treatment on (*i*) specific gravity, softening point (R and B), and boiling range of tar, (*ii*) volume of noncondensable gases formed, and (*iii*) alkali solubles in distillates up to 360°C. (atmospheric pressure) from the treated tar. Table 4 gives the composition of noncondensable gases formed during pressure treatment of tar.

TABLE 1—DISTILLATION OF HEAVY TAR UNDER PRESSURE

(Sp. gr. 28°/28°C., 1·05)

No.	Distillation pressure p.s.i.g.	Max. liquid temp. °C.	Max. vap. temp. °C.	Distillate oil yield (on dry basis) Vol. %	Properties of distillate fractions (Water-free)															R & B softening pt. of residue °C.
					Sp. gr. of distillate fractions (vol. %) at 28°C.			Alkali-solubles in distillate fractions (vol. %)			Hydrocarbon types in neutral oil from distillate (vol. %)									
											0-10			10-20			20-30			
					0-10	10-20	20-30	0-10	10-20	20-30	A	O	S	A	O	S	A	O	S	
1.	*Atmospheric	379	277	32·2	0·9961	0·9919	0·9919	32·0	34·0	31·0	60·9	13·3	25·8	68·1	13·2	28·7	64·4	2·1	33·5	41·5
2.	30	422	269	31·0	0·9367	0·9385	0·9319	25·0	24·0	21·0	63·0	11·0	26·0	59·1	11·3	30·6	50·6	6·2	43·2	62·5
3.	50	434	263	32·2	0·8742	0·9206	0·9183	19·0	21·0	19·0	46·3	13·5	40·2	47·9	13·6	38·5	50·0	11·2	38·8	81·0
4.	100	430	254	21·5	0·8200	0·8624	0·8867	18·3	18·0	..	..	..	..	..	..	..	..	..	..	83·0
5.	200	470	232	26·5	0·7886	0·8439	0·8997	20·0	20·0	18·0	21·5	13·0	65·5	31·8	9·5	58·7	39·7	12·1	48·2	Powder

A—Aromatics
O—Olefins
S—Saturates

*Atmospheric pressure at Hyderabad is 13·75–13·82 lb./sq. in.

TABLE 2—DISTILLATION OF LIGHT TAR UNDER PRESSURE
(Sp. gr. 25/25°C., 0·970)

	Distillation pressure, p. s. i. g.	
	Atmospheric	150
Max. temp., °C.		
Liquid	443	421
Vapour	303	298
Distillate oil yield (on dry basis), vol. %	72·3	60·0
Properties of distillate fractions (water-free)		
Sp. gr. of distillates at 28°C.		
0-10, vol. %	0·9208	0·9191
10-20 do	0·9304	0·9344
20-30 do	0·9396	0·9296
30-40 do	0·9410	0·9185
40-50 do	0·9404	0·9065
50-60 do	0·9417	0·8966
60-70 do	0·9484	0·9322
Alkali-solubles in distillates, vol. %		
0-10	40·7	37·3
10-20	40·3	44·0
20-30	43·1	42·1
30-40	35·0	35·8
40-50	28·0	24·0
50-60	26·0	22·6
60-70	17·3	17·3
Hydrocarbon types in neutral oils from distillates, vol. %		
0-30 Aromatics	55·0	53·9
Olefins	20·0	12·8
Saturates	25·0	33·3
30-60 Aromatics	56·6	47·5
Olefins	20·25	19·6
Saturates	23·1	32·9

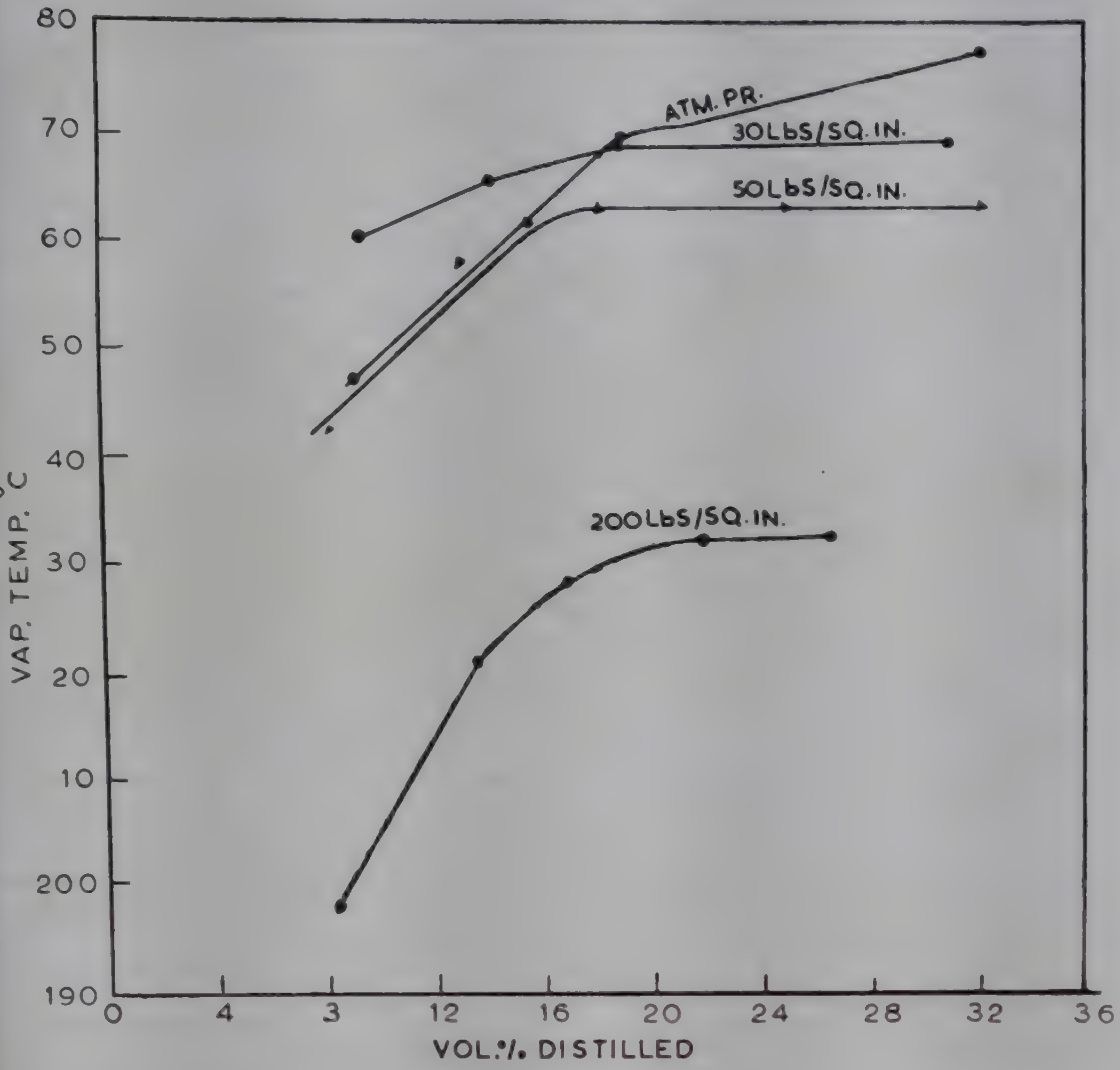

Fig. 2—Distillation characteristics of heavy tar at various pressures

Pressure Distillation. In the case of heavy tar it is seen (Fig. 2) that with increase in distillation pressure the elevation in boiling point, which is normally expected, does not take place except for the first portions distilled at 30 lb./sq. in. Generally, as the pressure is increased, the vapour temperature to obtain the same percentage of distillate decreases in spite of rise in liquid temperature, indicating formation of lower boiling fractions due to cracking. This phenomenon appears to be more pronounced as the pressure increases from 30-200 lb./sq. in. As seen from Table 2, there is a decrease in specific gravity, alkali soluble content and an increase in the softening point of the residue. The content of saturates in the neutral fractions steadily increases with distillation pressure with an approximately corresponding decrease in the aromatic content. The variation in the olefin content is very little.

In the case of light tar, however, the effect of increased distillation pressure is not so pronounced (Figs. 4 & 5). Although the vapour temperature

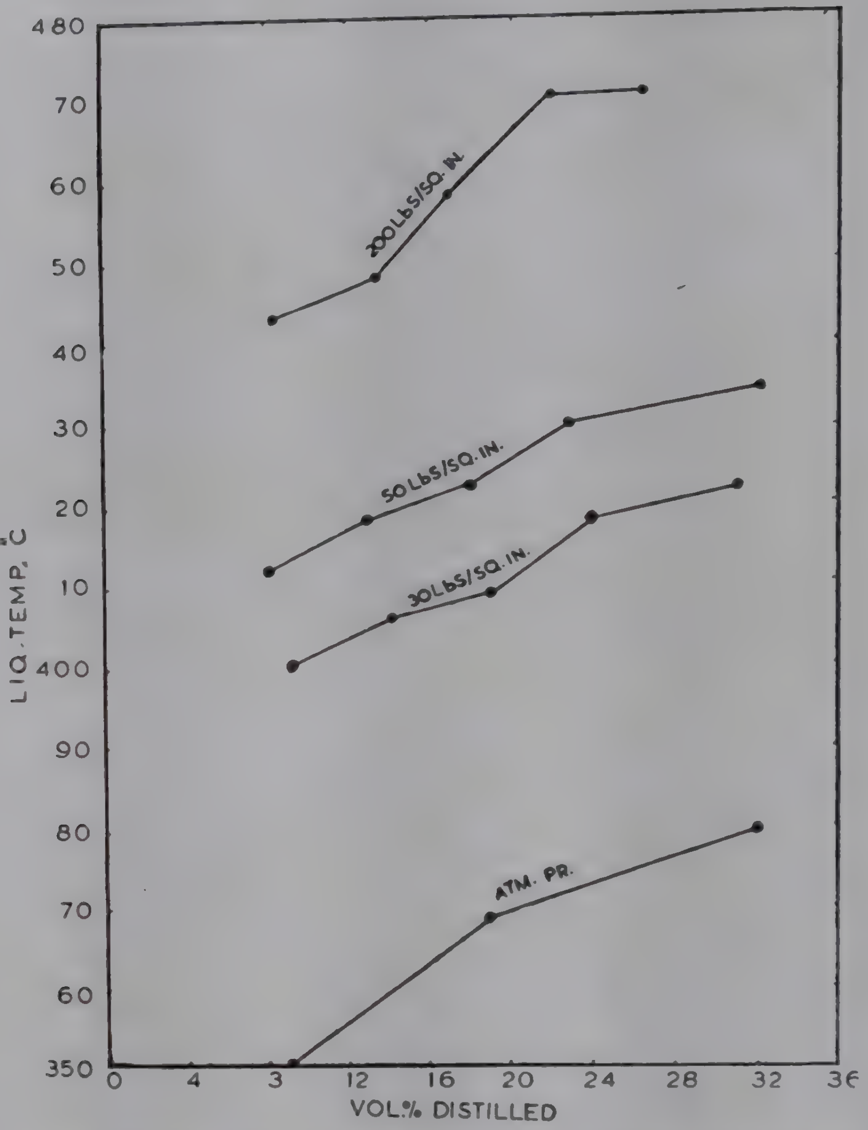

FIG. 3—LIQUID TEMPERATURE VS VOL. % DISTILLED AT VARIOUS PRESSURES FOR HEAVY TAR

at 150 lb./sq. in. is more than that at atmospheric pressure for the same per cent distilled, the difference in liquid and vapour temperature at 150 lb./sq. in. is disproportionately large which is indicative of cracking taking place. From Table 3 and Fig. 7 little change is noticeable in the specific gravity and boiling range of the first fractions (0-30 per cent); beyond this, however, there is considerable difference. Whereas the specific gravity of fractions (30-60 per cent) continue to rise at atmospheric pressure, there is a continuous decrease at 150 lb./sq. in. distillation pressure and their alkali soluble content is also less. This onset of cracking after the first fractions are removed indicates that the presence of low boiling oils (fractions 0-30 per cent) inhibits cracking, as observed by Weiss[2] for coke-oven tar. However, it is not clear why there is an increase in the saturates content of even the first fractions obtained at 150 lb./sq. in.

TABLE 3—PRESSURE TREATMENT OF HEAVY TAR

PRESSURE OF TREATMENT, p.s.i.g.	TIME OF TREATMENT, hr	TEMP. OF TREATMENT °C. (av.)		SP. GR. OF PRODUCT AT 28°C.	SOFTENING POINT OF PRODUCT °C.	DISTILLATE UP TO 360°C. %	SP. GR. OF DISTILLATE AT 28°C.	ALKALI SOLUBLES IN DISTILLATE %	SOFTENING POINT OF PITCH ABOVE 360°C.	BENZENE INSOLUBLES IN PRODUCT	AMOUNT OF NONCONDENSABLES, litres
		Liquid	Vapour								
Untreated tar	..	..	..	1·072	22·5	38·0	1·0070	31·0	48·5	0·5230	..
Atmospheric	6	300	100	1·070	32·5	48·0	0·9963	32·7	66·5	1·8390	..
250	0	409	159	1·081	28·2	32·5	..	..	58·0	3·5730	2·2
200	2	350	154	1·085	28·0	34·0	0·9811	29·0	64·0	3·7870	..
200	6	315	126	1·081	26·0	41·0	0·9851	28·0	69·5	3·9460	3·5
200	24	310	142	1·079	25·0	44·4	0·9761	28·0	75·0	5·9230	4·5

TABLE 4—COMPOSITION OF NONCONDENSABLE GASES FORMED DURING THE PRESSURE TREATMENT OF HEAVY TAR AT 200 lb./sq. in.

DURATION OF TREATMENT, hr	VOL. OF GASES FORMED, litres	CO_2	UNSATURATES	O_2	CO	H_2	SATURATES	N_2	CARBON NUMBER
6	3·0	10·2	5·1	1·4	4·9	5·3	69·3	3·8	1·46
24	4·5	16·0	5·6	1·6	4·0	13·6	57·67	1·53	1·67

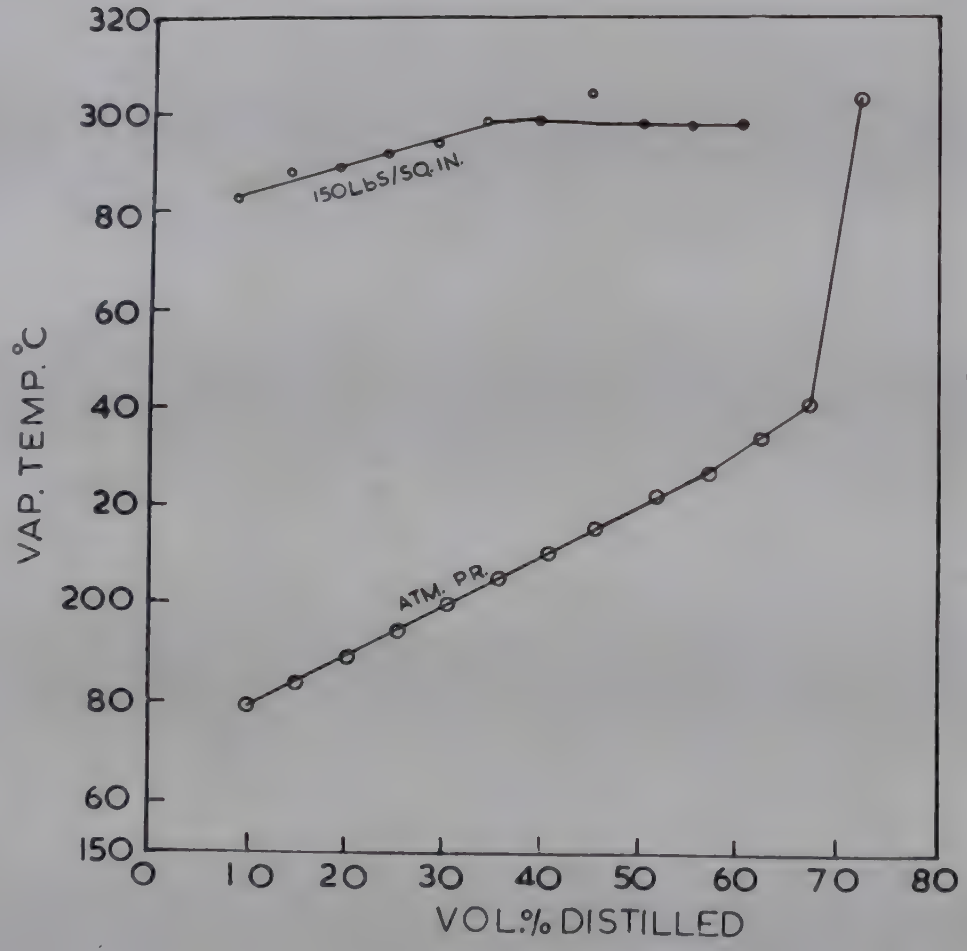

Fig. 4—Distillation characteristics of light tar at atmospheric and 150 lbs/sq. in.

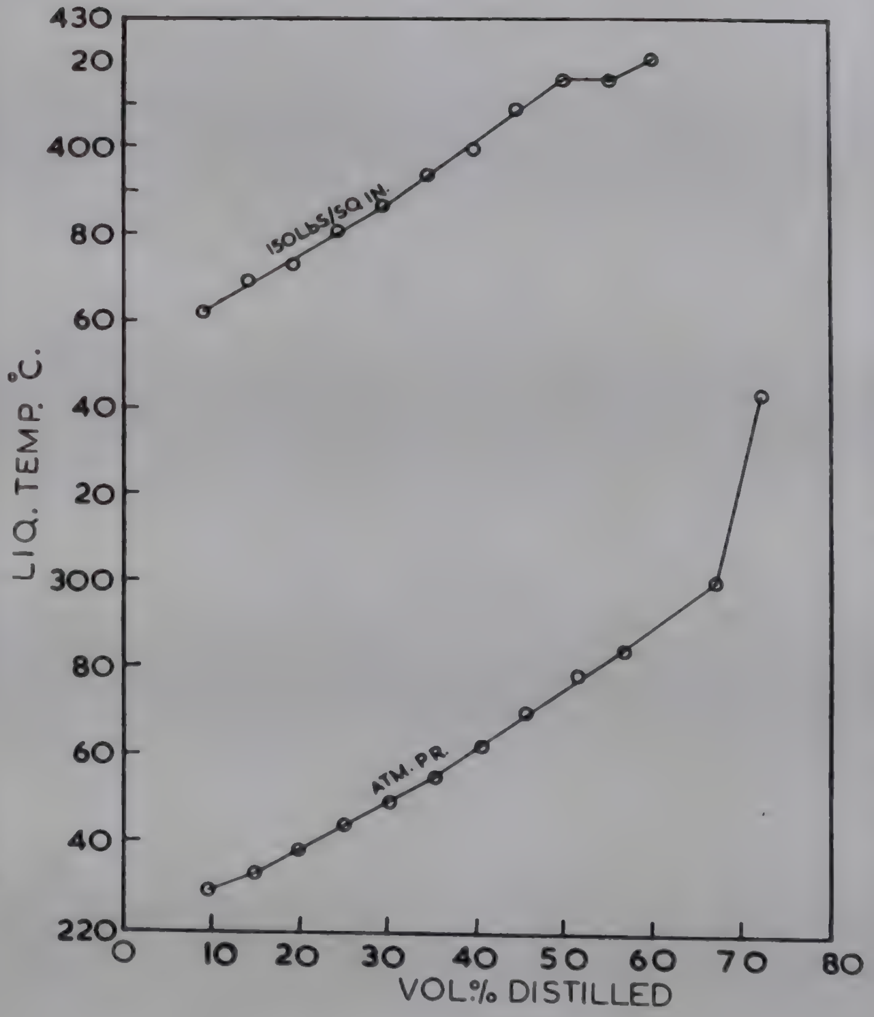

Fig. 5—Liquid temperature vs vol. % distilled at atmospheric and 150 lbs/sq. in. for light tar

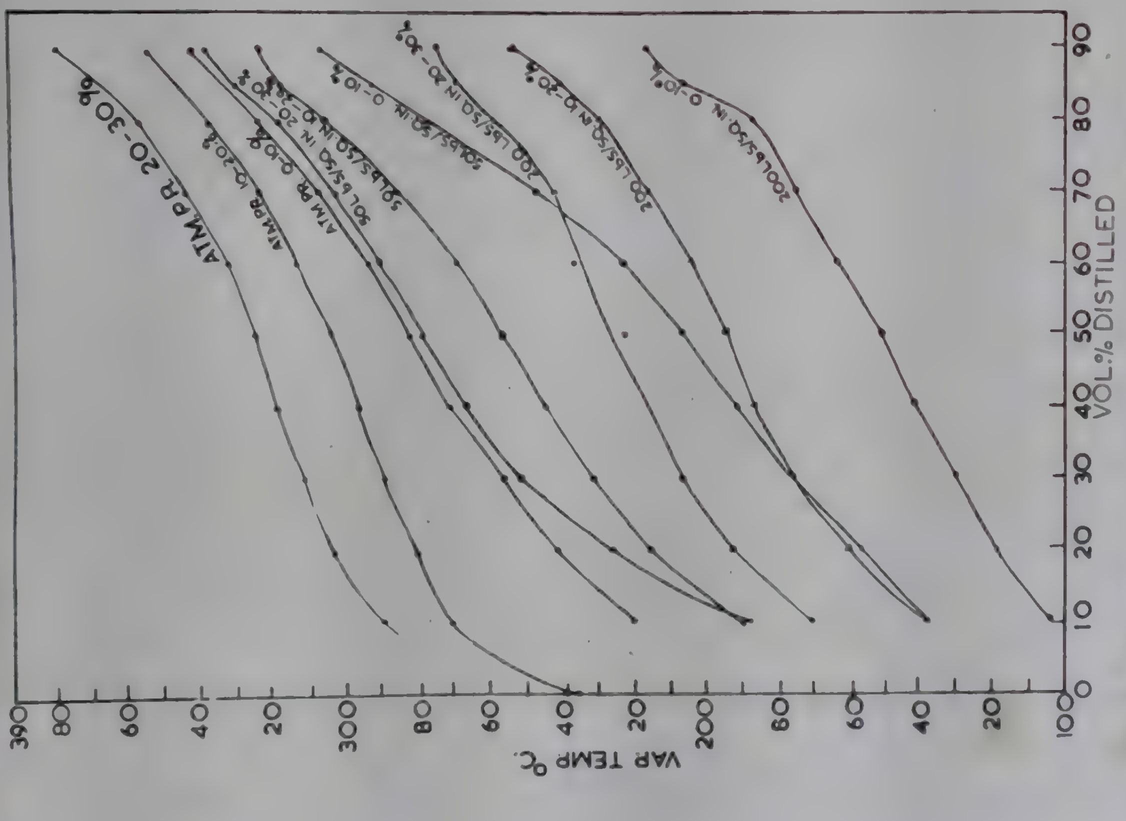

FIG. 6—BOILING RANGE AT ATMOSPHERIC PRESSURE OF FRACTIONS FROM HEAVY TAR DISTILLATION UNDER PRESSURE

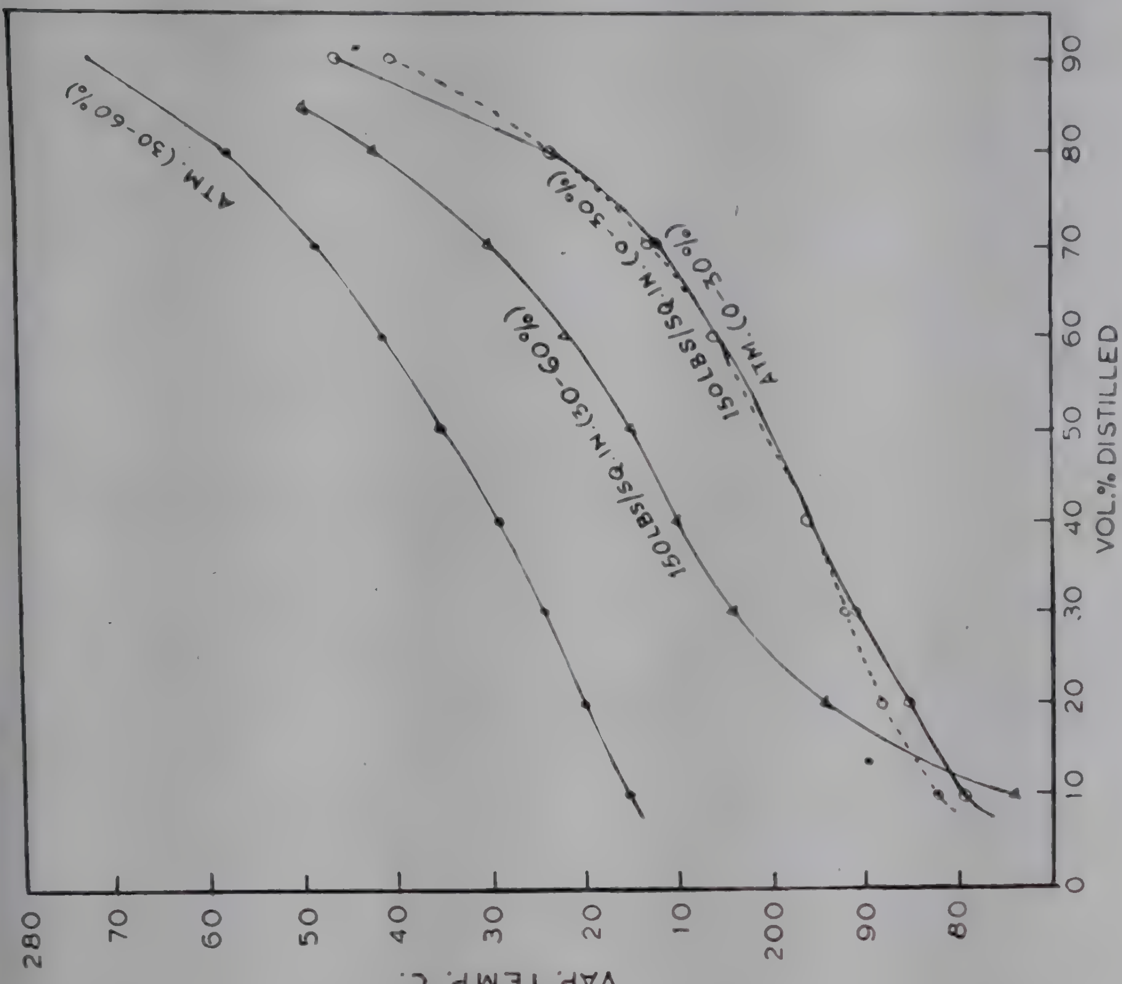

FIG. 7—DISTILLATION CHARACTERISTICS OF DISTILLATES FROM LIGHT TAR DISTILLATION UNDER PRESSURE

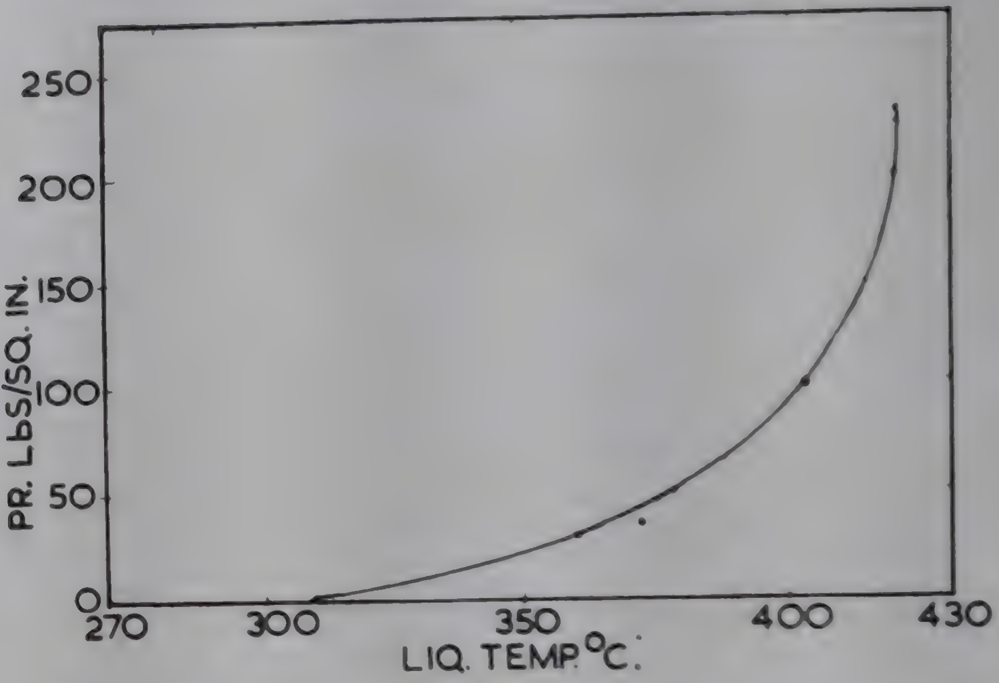

FIG. 8—VARIATION OF PRESSURE WITH LIQUID TEMPERATURE DURING TREATMENT OF HEAVY TAR AT 200 LBS/SQ. IN.

Pressure Treatment. Table 3 shows that on heating heavy tar under a pressure of 200 lb./sq. in. for 2 to 24 hr, its specific gravity increases in the beginning from 1·072 to 1·085 and then gradually decreases to 1·079 during the course of 22 hr. With increase in the duration of treatment there is a slight fall in the average liquid temperature. The increase in the amount of benzene-insolubles and quantity and composition of noncondensable gases formed indicate increased degree of Pyrolysis. The carbon number of the gas increased from 1·46 for 6 hr treatment to 1·67 for 24 hr treatment. The specific gravity and alkali solubles content of distillate fraction up to 360°C. from pressure-treated tar are less than those of fractions from untreated tar and they also continue to decrease with increased duration of treatment.

Fig. 8 shows that during pressure treatment the rise in pressure is steady in the beginning with increase in liquid temperature, but after about 410°C. there is a sudden rise in pressure with little increase in liquid temperature owing to sudden increased evolution of noncondensable gases. A similar observation is also made for coke-oven tar by Weiss[2].

ACKNOWLEDGEMENT

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Catalytic Cracking of Some Low Temperature Tar Fractions

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Jealgora

Catalytic cracking of some neutral oil fractions of middle oil obtained from Lurgi-Spuelgas low temperature carbonization pilot plant in operation at the Regional Research Laboratory, Hyderabad, has been studied over silica-alumina and active carbon catalysts. The liquid products have much lower viscosity and initial boiling point than the feed and contain substantial amount (up to 50 per cent) of distillates below the boiling range of feed. With increasing reaction temperature the yield of liquid products decreases while that of gas increases. The reaction products are more aromatic than the feed. No change in viscosity and specific gravity of the product was observed for a storage period of one month. Recycling of the reaction products over fresh catalyst did not make any significant change in the yield of lighter products showing that the products are refractory to further cracking under given conditions. Analysis of products shows that splitting of the side chain, dehydrogenation and, to some extent, condensation are the main reactions in the case of silica-alumina catalyst. With active carbon the increase in the aromatic content of reaction products is not observed up to a reaction temperature of 500°C.

The economics of low temperature carbonization (l.t.c.) depend to a great extent on the financial returns from the byproducts. Proper utilization of the l.t. tar is therefore important. The tar acids and bases have many commercial uses while the neutral oil is now gaining importance as good starting material for synthetic petrol production. The various aspects of the problem of producing diesel fuels from neutral oils have been under investigation at the Central Fuel Research Institute for some time and, as part of this scheme, the suitability of cracking processes used in petroleum industry, for converting some of the heavier fractions to lighter and more useful components is reported in this paper.

A number of foreign patents claim production of a variety of products like liquid fuels, aromatics, fuel gases and olefinic gases from thermal cracking of l.t. tar[1]. From Japan, Suzuki *et al.*[2] have reported work on thermal cracking of l.t. tar fractions in a continuous pilot plant in order to get solvent naphtha fractions. For obtaining olefins by thermal cracking of heavy fractions, Kishida and Chuto[3] claimed the best yield at 700°C. and 10 mm. Hg pressure; the yields of ethylene and propylene were 10·3 and 8·6 per cent respectively.

Very little work has been published on the catalytic cracking of l.t. tar fractions. Kobayashi[4] has studied contact refining and distillation with Japanese acid clay. Kuczynski[5,6] reported the catalytic cracking of Polish oils obtained from brown-coal tars over synthetic aluminium silicate catalysts. By cracking 180 – 280°C. fraction at 400°C., the yield of light oil was about 25 per cent.

EXPERIMENTAL

The cracking studies were conducted over a fixed catalyst bed in the apparatus shown in Fig. 1 and consisting essentially of a calibrated constant rate feeder, a vertical glass reactor enclosed in a furnace having preheater and catalyst zones, and a product recovery system for collecting the liquid and gaseous reaction products. The reactor furnace has an independent arrangement for heating, controlling and recording the temperature of the two zones. Tar oil feed from the top flows down by gravity and is vaporized in the upper part of the reactor which is filled with glass beads and kept above the final boiling point of the feed. The vapours then pass over the catalyst maintained at the desired reaction temperature.

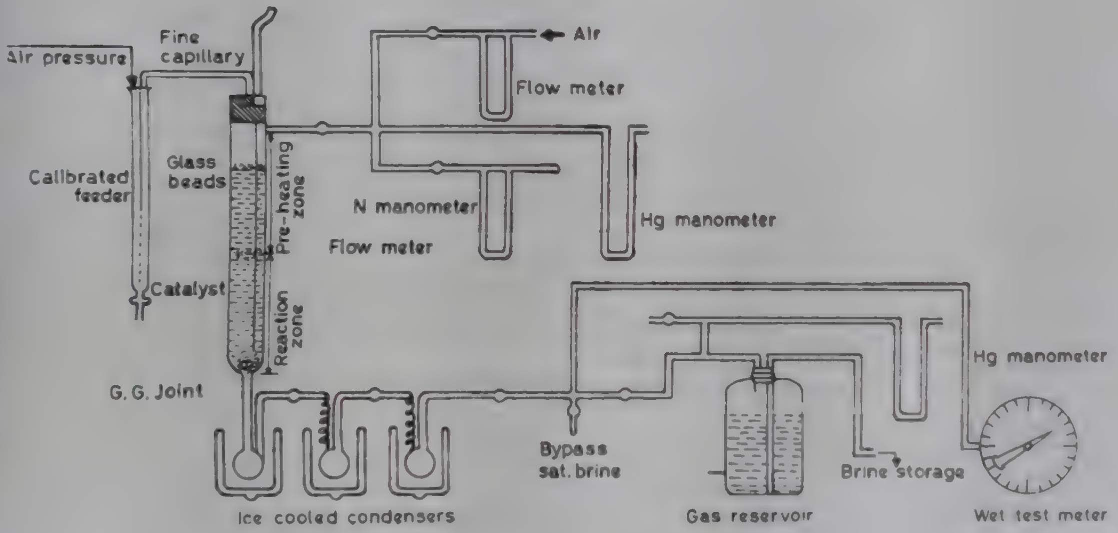
Air pressure
Fine capillary
Air
Flow meter
Calibrated feeder
Glass beads
Pre-heating zone
N manometer
Flow meter
Hg manometer
Catalyst
Reaction zone
G. G. Joint
Hg manometer
Bypass sat. brine
Brine storage
Ice cooled condensers
Gas reservoir
Wet test meter

FIG. 1—APPARATUS FOR CATALYTIC CRACKING

Before the start of a run and at the end the system is flushed with nitrogen for 15-20 min. to remove all the hydrocarbon vapours.

After the experiment, all the liquid products in the various receivers were collected together and analysed for gravity, viscosity, distillation characteristics and hydrocarbon group composition. Olefins were determined by absorption in 84 per cent sulphuric acid and olefins plus aromatics by shaking with Kattwinkel reagent (70 wt per cent sulphuric acid; 30 wt per cent phosphorus pentoxide) at 0°C. In a few cases the analysis of gaseous products was also carried out.

At the end of each run the catalyst was fully reactivated by burning all the carbon deposited on the catalyst with air at 550-600°C. for 12 hr or more.

MATERIALS

In the Lurgi-Spuelgas l.t.c. plant the byproduct recovery system is such that the vapours are condensed in three stages, as light oil, middle oil and heavy tar. The middle oils from carbonization of Upper Kajora and Jambad-Bowlah coals was used as the starting material for this work. The middle oil was distilled into appropriate cuts and the fractions freed of tar bases and tar acids by extraction with sulphuric acid and sodium hydroxide respectively followed by washing with water and dehydration.

Co-precipitated silica-alumina catalyst containing 10 per cent Al_2O_3 was prepared from sodium silicate and aluminium nitrate and made into granules of 6-10 mesh size.

Active carbon prepared by passing air-steam mixture over low temperature char for 2 hr at about 700°C. was also used as catalyst.

DATA AND DISCUSSION

The analysis of the neutral oil fractions used as the feed stock is given in Table 1. In Tables 2-5 the data from cracking runs are reported. Each series of runs was carried out by varying only the temperature of catalyst keeping contact time and total feed, i.e. duration of the run constant. For study of influence of space velocity the temperature and total feed were kept constant.

The catalytic cracking of the Upper Kajora neutral oil fraction (300-360°C.) over silica-alumina catalyst did not show much conversion at temperatures ranging 450-480°C., but at 500°C. and above substantial amounts of lighter hydrocarbons were obtained (Table 2). At very high temperatures the yield of the liquid product boiling below 300°C. again decreases due to excessive cracking to gas as well as the formation of condensed products of boiling range above that of the feed. The yield of liquid products decreases continuously with rise of reaction temperature, while the amount of gas formed increases progressively (Fig. 2). The change in the respective yields of these two products is very marked as the catalyst temperature goes from 540 to 560°C. The initial boiling point of the liquid

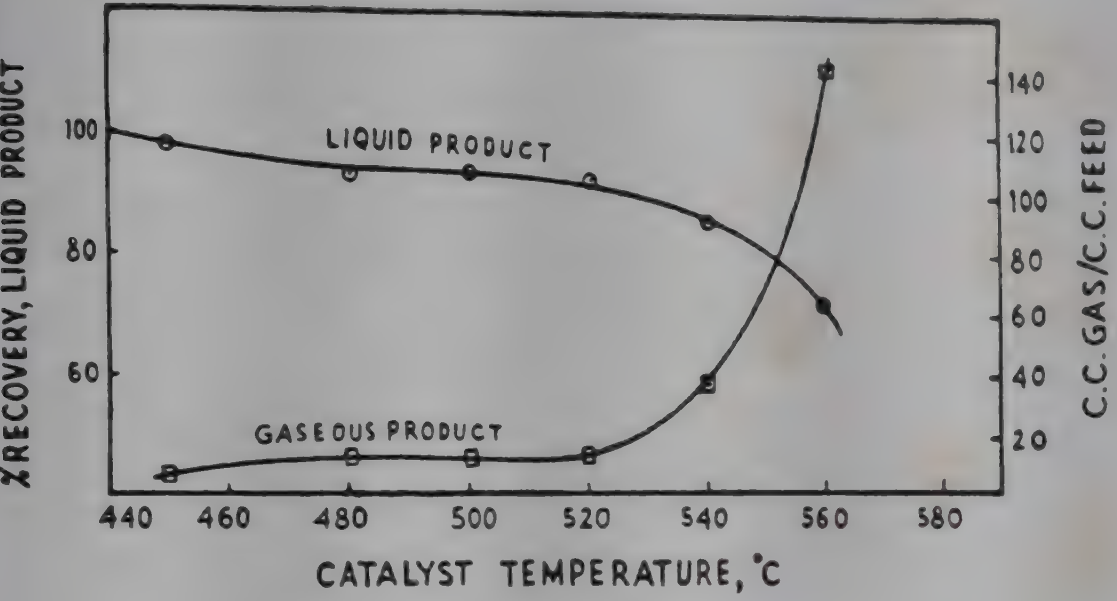

FIG. 2—YIELD OF LIQUID AND GASEOUS PRODUCTS

TABLE 1—CHARACTERISTICS OF THE FEED STOCK

	UPPER KAJORA 270-300°C.	NEUTRAL OIL 300-360°C.	JAMBAD-BOWLAH NEUTRAL OIL 270-300°C.
Sp. gr. 60°/60°F.	0·9012	0·925	0·917
Carbon residue (Conradson)	0·03	0·05	..
Kinematic viscosity, CS at 100°F.	3·637	7·79	3·55
Composition, %			
Olefins	13·0	14·0	12·0
Aromatics	59·0	57·0	63·0
Saturates	28·0	29·0	25·0
Ultimate analysis, %			
Carbon	87·05	86·50	..
Hydrogen	11·41	11·00	..
Sulphur	0·28	0·23	..
Nitrogen	0·25	0·23	..
Calorific value B.t.u./lb.	18,660	18,500	..
Average mol. wt	233·0	304·0	..

TABLE 2—CATALYTIC CRACKING OF UPPER KAJORA NEUTRAL OIL FRACTION 300-360°C.
[Catalyst: Al_2O_3-SiO_2 (10% Al_2O_3); LHSV=0·49-0·50; Duration of run: 2 hr]

RUN No.	CATALYST TEMP. °C.	YIELD OF LIQUID PRODUCTS vol. %	GASEOUS PRODUCTS cc./cc. feed	DISTILLATION OF LIQUID PRODUCT			CHARACTERISTICS OF DISTILLATE				
				I.B.P. °C.	% Distillate up to		Sp. gr. 60°/60°F.	Viscosity Cs. at 100°F.	Composition, vol. %		
					300°C.	360°C.			Aromatics	Olefins	Saturates
Original feed	..	..	..	..	..	..	0·9247	7·79	51	14	29
1.	450	97·7	7·7	130	22·3	81·2	0·9113	5·44	56	11	33
2.	480	93·5	13·6	130	27.9	80·0	0·9118	4·86	57	9	34
3.	500	93·4	13·3	130	35·0	94·0	0·9088	4·10	57	12	31
4.	520	92·8	12·5	122	..	..	0·9126	3·91	64	9	27
5.	540	85·2	36·8	110	60·0	90·0	0·9186	3·64	65	12	23
6.	560	71·3	141·0	82	50·0	83·9	0·9143	2·17	66	12	22

TABLE 3—CATALYTIC CRACKING OF UPPER KAJORA NEUTRAL OIL FRACTION 270-300°C.
[Catalyst: Silica-Alumina (10% Al_2O_3, Copptd.); LHSV=1·02; Duration of run=2 hr]

RUN No.	CATALYST TEMP. °C.	YIELD OF LIQUID PRODUCTS vol. %	GASEOUS PRODUCTS cc./cc. feed	DISTILLATION OF LIQUID PRODUCTS			CHARACTERISTICS OF DISTILLATE				
				I.B.P., °C	Distillation up to 270°C.	Final boiling point (F.B.P.), °C.	Sp. gr. 60/60°F.	Viscosity Cs. 100°F.	Composition, vol. %		
									Aromatics	Olefins	Saturates
Original feed	..	..	..	..	..	..	0·904	3·64	58	13	29
1.	450	95·5	..	160	43·4	330	0·895	2·93	..	..	..
2.	480	95·7	..	130	49·0	330	0·900	2·95	69	8	23
3.	520	90·8	..	120	49·0	324	0·897	12·58	62	6	32
4.	540	93·0	..	130	43·5	290	0·899	2·65	66	9	25

product decreases as the cracking temperature is raised (Fig. 3). There is only a slight decrease in the specific gravity of the distillate but a marked and progressive lowering of the viscosity is observed along the entire series (Fig. 4). The composition of the distillate shows a steady and gradual increase in aromatic content, higher reaction temperature giving greater conversion to aromatics (Fig. 5). Surprisingly, there is not much change in the olefin content of the liquid products of different runs. In this boiling range (300-360°C.) the material consists mostly of complex molecules containing aromatic and naphthenic rings with paraffinic side chains and the analysis carried out only denotes portions with a particular structure predominating. The estimation by Kattwinkel reagent is a measure of the portion which contains molecules in which aromatic rings predominate although these may contain paraffin side chains or even naphthenic rings. The increase in the amount of aromatics, therefore, indicates cracking of paraffins (free or side chains) mostly to gas and also dehydrogenation of naphthenes.

The cracking of the 270-300°C. neutral oil fractions follows nearly the same pattern with respect to yield of products at various temperatures as well as composition of reaction products (Table 4). But conversion to lighter constituents is less under a given set of conditions than that obtained from 300-360°C. cut. The stability of the molecule decreases with increase in molecular size and the lighter molecules are more resistant to cracking.

Compared with silica-alumina, the active carbon catalyst gives lower conversions at the same reaction temperatures (Table 5). At 500°C. the yield of the lighter fraction is 45 per cent with active carbon and 57 per cent with silica-alumina. Probably active carbon catalyst needs much higher

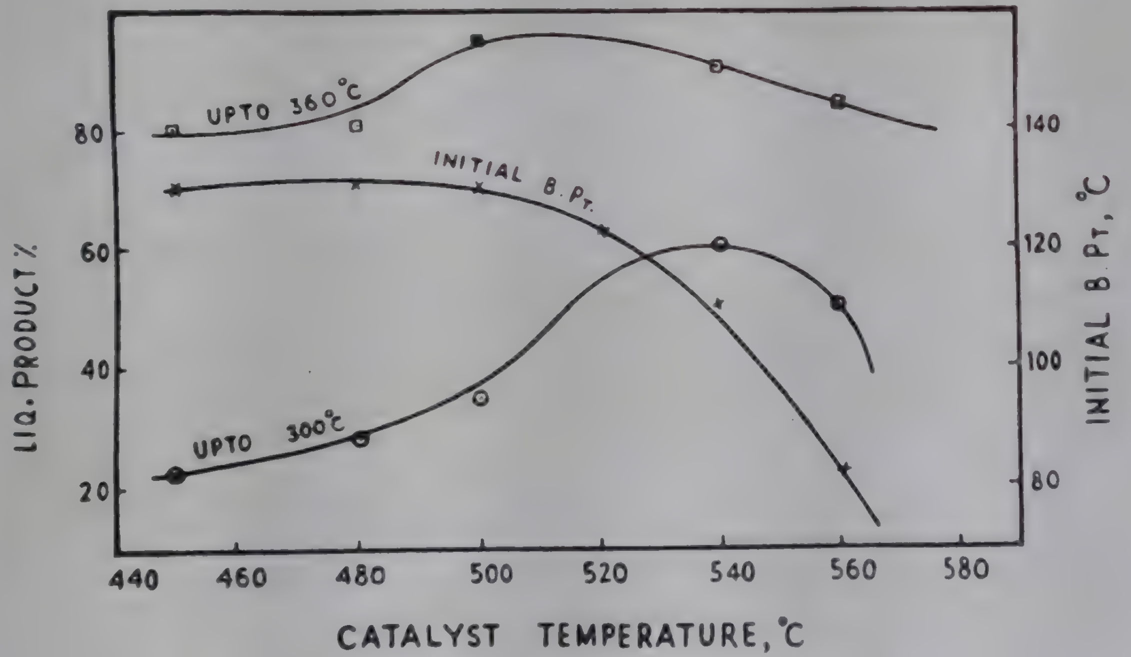

FIG. 3—DISTILLATION CHARACTERISTICS OF LIQUID PRODUCTS

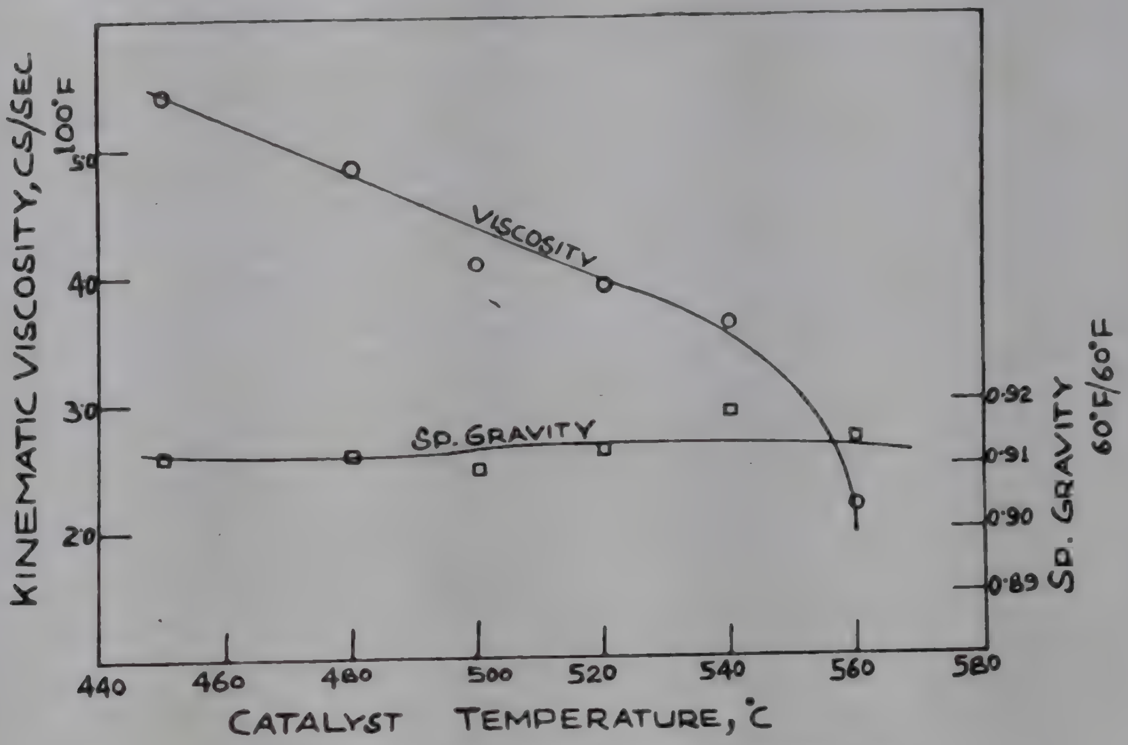

Fig. 4—Viscosity and specific gravity of distillate

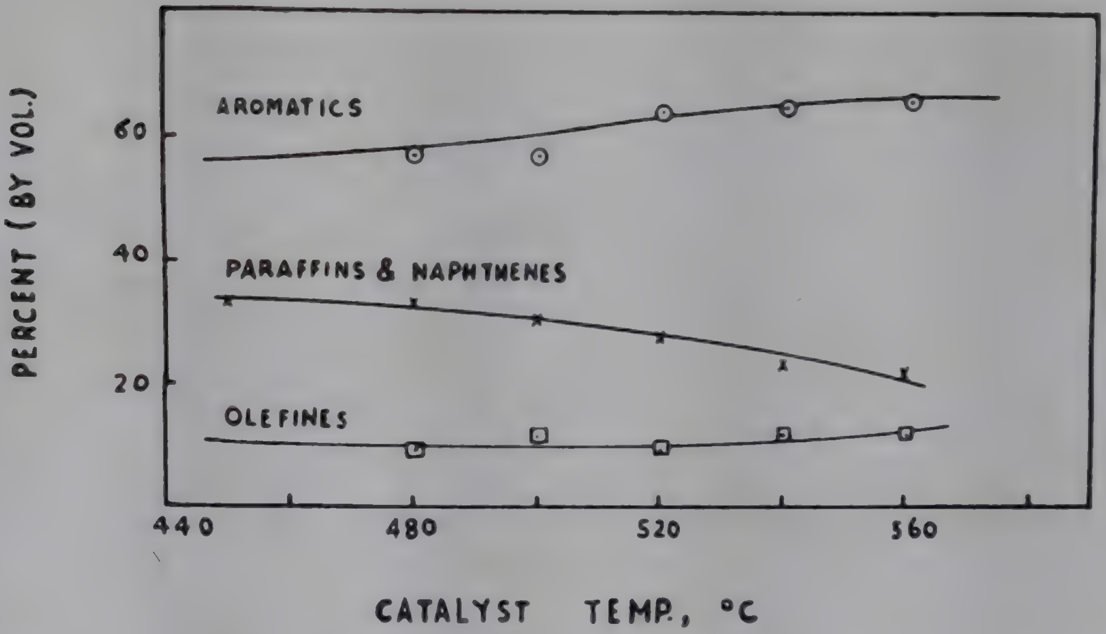

Fig. 5—Composition of distillate

reaction temperature to obtain equivalent results. A noteworthy feature of this catalyst is that aromatics in the products do not increase with reaction temperature but on the other hand, decrease to a small but definite extent. Olefins, again, do not vary much and so the net result is a rise in the paraffinic and naphthenic portion. Unlike the silica-alumina the active carbon catalyst was not reactivated without any intermediate treatment.

TABLE 4—CATALYTIC CRACKING OF JAMBAD-BOWLAH MIDDLE OIL FRACTION 270-300°C.

[Catalyst: Silica-Alumina (Aluminium—10% Al_2O_3); LHSV=0·51; Duration of run=2 hr]

RUN No.	CATALYST TEMP. °C.	YIELD OF LIQUID PRODUCT vol. %	GAS FORMED cc./cc. feed	DISTILLATION OF LIQUID PRODUCT				CHARACTERISTICS OF LIQUID PRODUCT				
										Composition, vol. %		
				I.B.P. °C.	Vol. % up to 270°C.	F.B.P. °C.	Total distillate %	Sp. gr. 60/60°F.	Viscosity Cs. at 100°F.	Aromatics	Olefins	Saturates
Original feed	..	..	..	..	..	..	..	0·917	3·55	63	12	25
1.	460	97·8	9·5	120	48·8	326	91·1	0·905	3·13	63	8	29
2.	480	97·6	13·5	130	48·8	328	91·6	0·904	2·94	69	8	23
3.	500	92·8	32·9	130	56·8	325	92·0	0·903	2·75	71	7	22
4.	520	90·7	45·5	130	50·6	325	90·3	0·907	2·65	..	..	..
5.	540	84·7	48·2	130	48·6	295	80·5	0·904	2·10	71	8	20

TABLE 5—CATALYTIC CRACKING OF JAMBAD-BOWLAH NEUTRAL OIL FRACTION 270-300°C.

(Catalyst: Activated coke; LHSV=0·4; Duration of run=2 hr)

RUN No.	CATALYST TEMP. °C.	YIELD OF LIQUID PRODUCT vol. %	GAS FORMED cc./cc. feed	DISTILLATION OF LIQUID PRODUCT				CHARACTERISTICS OF LIQUID PRODUCT				
										Composition, vol. %		
				I.B.P. °C.	% up to 270	F.B.P. °C.	Total distillate %	Sp. gr. 60/60°F.	Viscosity Cs. at 100°F.	Aromatics	Olefins	Saturates
Original feed	..	..	..	..	..	..	..	0·907	3·96	67	9	24
1.	420	98·8	5·0	130	34·8	328	95·3	0·906	3·57	61	12	27
2.	440	98·2	10·9	136	34·4	326	96·0	0·906	3·61	59	12	29
3.	460	98·1	18·9	100	39·2	326	92·8	0·903	3·26	62	12	26
4.	480	98·4	—	104	41·6	327	94·0	0·906	3·31	58	14	28
5.	500	91·8	22·7	78	45·5	320	93·5	0·912	2·97	58	14	28

The analysis of gaseous products from some of the runs showed that they consisted mostly of unsaturated constituents. A typical composition of the gaseous products from a run at 540°C. over active carbon was:

	Vol. %
Unsaturated hydrocarbons	66·7
Methane	13·9
Ethane	9·9
Hydrogen	3·7
Carbon monoxide	3·6
Carbon dioxide	2·3
	100·1

The cracking of 300-350°C. neutral oil fraction of Jambad-Bowlah middle oil was also studied over active carbon catalyst at a LHSV of 1·25 in the temperature range 480-560°C. There was very little change in the composition of the products and most of the feed was recovered unreacted.

In order to examine the effect of recycling the reaction products, a series of runs were conducted using products from one run as a feed for the next. The recycling was done thrice, activating the catalyst every time (Table 6). While appreciable conversion was obtained for the first run, the subsequent recycling gave little further change in the yield of lighter fractions. Thus the products of cracking are quite refractory to further cracking under similar reaction conditions.

The gravity and viscosity of liquid reaction products from a typical cracking run over silica-alumina catalyst were checked at intervals for a storage period of one month to ascertain whether the main reaction during

TABLE 6—EFFECT OF RECYCLING REACTION PRODUCTS

[Feed: Upper Kajora Neutral Oil Fraction 300-360°C.; Catalyst: Silica-Alumina (10% Al_2O_3)]

CATALYST TEMP. °C.	LHSV cc./hr/cc.	YIELD OF LIQUID PRODUCTS vol. %	GASEOUS PRODUCTS cc./cc. feed	LIQUID PRODUCTS	
				Sp. gr. 60/60°F.	Kinematic viscosity Cs at 100°F.
Original feed	..	..	..	0·9247	7·79
500	0·50	96·6	23·9	0·9133	4·76
500	0·50	94·5	20·8	0·9125	4·17
500	0·50	94·6	18·9	0·9126	3·86
500	0·50	93·4	19·3	0·9105	3·46

TABLE 7—CHANGE IN CHARACTERISTICS OF REACTION PRODUCTS ON STORAGE

PERIOD OF STORAGE	SP. GR.	KINEMATIC VISCOSITY Cs at 100°F.	% INCREASE IN VISCOSITY
Fresh sample	0·8999	2·822	..
14 days	0·8999	2·831	0·32
22 days	0·8999	2·838	0·57
29 days	0·8974	2·846	0·85
36 days	..	2·851	1·03

the cracking is just thermal depolymerization followed subsequently by polymerization again on keeping for sufficient interval. No significant change in viscosity of the cracked product was observed for one month (Table 7), indicating the absence of any such change during this period.

The study shows that while it is possible to get up to 50 per cent of lighter fractions by catalytic cracking of the l.t. tar fractions, the already low diesel index of the feed falls further and the products have higher aromatic contents. While this is good when the aim is to obtain low molecular weight aromatics, hydrogenation of the aromatics will be necessary to obtain diesel oils. Alternatively, hydrocracking may also be a suitable method of treatment.

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Thermal Cracking of Low Temperature Coal Tars

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Studies on thermal cracking of various low temperature tar fractions containing different amounts of tar acids at temperatures of 450-900°C. showed that the gas contained maximum unsaturates (49·6 per cent) at a cracking temperature of 550°C. and this depended on the tar acid content of the feed. The content of aromatics in the liquid product increased with an increase in cracking temperature. A temperature of 550°C. was found to be optimum for maximum process yields. High coke yield was found when tar acids were cracked at 700°C.

Cracking processes are of great importance in the petroleum industry for the production of gasoline from high-boiling fractions. The necessity to develop these cracking processes has been caused by an increasing demand for the various products, particularly for high octane gasoline and olefinic gases for the chemical industry. Thermal cracking process first commercialized in 1913 has been more or less completely replaced by catalytic cracking processes, though they are still retaining some of their importance for the production of olefinic gases for the petrochemical industry. In addition to gasoline of high octane value, catalytic cracking also produces large quantities of olefinic gases which can either be used for the production of polymer gasoline or for chemical industry. Cracking processes can also be successfully applied to coal tars for the production of motor fuel, olefinic gases, fuel gas, and low boiling tar acids which form raw materials for the manufacture of plastics, resins, disinfectants, etc. from high boiling tar acids.

Morrell and Egloff[1] obtained motor fuel by heat and pressure distillation of low temperature (l.t.) tar. Subsequently Egloff *et al.*[2] reported the results of pilot plant studies on cracking of l.t. tar, lignite tar, creosote oil, etc. Kishida and Chuto[3], obtained best yields of gaseous olefins by thermal cracking of heavy oil fractions of l.t. tar in steel vessels at 700°C., and —10 mm. Hg. Most of the work on cracking of tars is covered by patents. The present work on cracking of l.t. tars produced in the Lurgi-Spuelgas low temperature carbonization pilot plant, is undertaken with a view to find out the feasibility of producing unsaturated hydrocarbon gases and low boiling aromatics.

APPARATUS

The apparatus (Fig. 1) consisted of a silica tube furnace, 37 mm. internal diam. and 60 cm. long, heated by nichrome wire. The reactor was 22 mm. i.d. silica tube. The temperature inside the reactor was recorded by a thermocouple. Microfeed pump or alternately a constant head gravity flow system was used to feed the raw materials into the reactor. The liquid product was condensed in a series of receivers cooled by freezing mixture and the gas was collected in a gas holder at constant pressure.

EXPERIMENTAL PROCEDURE

Pure nitrogen was passed to purge air from the system while the furnace was heated. When the desired temperature was reached, nitrogen was stopped and the condensing system was connected to the gas holder. When the gravity flow system was used, the stop-cock was carefully adjusted to get the required flow rate of the feed. After the process period (1-2 hr) the furnace was maintained at the same temperature for about 5 min. to allow the liquid to pass into the reaction zone. After cooling down the furnace to about 250°C., nitrogen was passed through the system to expel

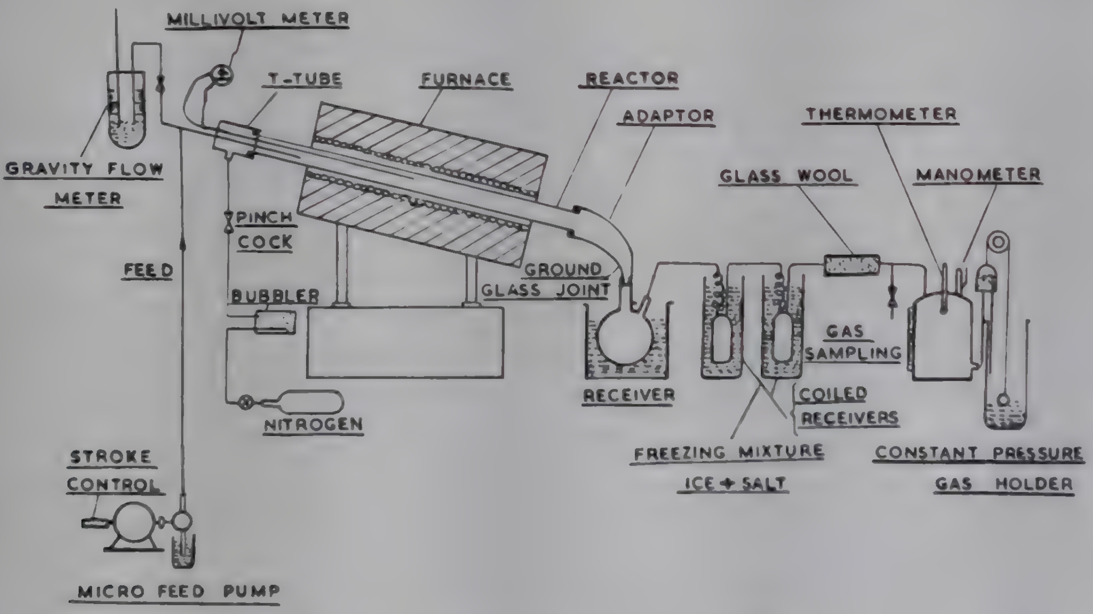
MILLIVOLT METER
T-TUBE
FURNACE
REACTOR
ADAPTOR
THERMOMETER
GRAVITY FLOW METER
GLASS WOOL
MANOMETER
PINCH COCK
FEED
GROUND GLASS JOINT
BUBBLER
GAS SAMPLING
RECEIVER
COILED RECEIVERS
NITROGEN
STROKE CONTROL
FREEZING MIXTURE ICE + SALT
CONSTANT PRESSURE GAS HOLDER
MICRO FEED PUMP

Fig. 1—Flow-diagram of apparatus

the last traces of reaction products remaining in the reactor into the gas holder.

Distillation data, specific gravity, tar acids and hydrocarbon types were determined in the liquid product. Coke deposit was estimated as benzene insolubles plus the coke determined by combustion method. The composition of the gas was determined.

MATERIALS

The following feed materials were used in these investigations. Their analyses are given in Table 1.

(*a*) Light tar distillate (b.p., 210-360°C.) containing 23 vol. % tar acids; (*b*) Light tar distillate containing 49 vol. % tar acids; (*c*) Neutral oil from (*a*); and (*d*) tar acids from (*a*).

RESULTS AND DISCUSSION

The above-mentioned feed materials were subjected to cracking at temperatures ranging from 450 to 900°C. maintaining the flow rate at 24 cc./hr. The results from thermal cracking of neutral oil are given in Table 2 and Fig. 2. The composition of the gaseous products from the remaining feed materials is given in Table 3.

The results show that in the case of neutral oil the yields of liquid products decreased from 97·07 per cent at 450°C. to 2·76 per cent at 900°C. The increase in specific gravity of the liquid products with the increase in temperature is also reflected in higher per cent of aromatics. Chromatographic analysis of liquid products indicated a decrease in saturates from 30·6 per cent in the feed to zero at 550°C., and a progressive decrease of olefins with the rise in cracking temperature. The aromatic content in the liquid product increased from 57·4 per cent in the feed to 92·2 per cent at 550°C. Further increase in temperature did not produce any noticeable effect. The increased yields of aromatics at higher temperatures are possibly due to the condensation reactions of olefins (formed from paraffins as also the ones originally present) and diolefins (products from olefins only) to cyclic unsaturates which get dehydrogenated to aromatics.

The content of saturates in the gaseous product decreased from 56·3 to 42 per cent as the temperature of cracking is increased from 450 to 550°C. However, from 550 to 700°C., there was a progressive rise from 42 to 65·3 per cent in and then a sudden decrease to 38·7 per cent on further rise in temperature. The per cent of unsaturates in the gases increased from 41·5 to 49·6 per cent at 550°C. and then rapidly decreased to 1·3 per cent at 900°C.

Such results may be expected from the thermal cracking of neutral oil containing a complex mixture of different types of hydrocarbons—

TABLE 1—ANALYSIS OF DIFFERENT FEEDS

Feed	A.S.T.M. B.P. range	Sp. gr. at 30°C.	Tar acids vol. %	Tar bases wt %
Light tar distillate	210-360°C. (86·7%)	0·9521	23·0	3·92
Light tar distillate	220-360°C. (80·0%)	1·008	49·0	2·80
Neutral oil*	206-360°C. (96·0%)	0·9126	..	..
Tar acids	223-340°C. (51·2%)	1·0903	100·0	..

*Neutral oil composition (vol. %); saturates 30·6, olefins 12·0, aromatics 57·4.

TABLE 2—THERMAL CRACKING OF NEUTRAL OIL

Temp. of cracking, °C.	450	500	550	600	700	800	900
Feed flow rate, cc./min.	0·4	0·4	0·4	0·4	0·4	0·4	0·4
Process period, min.	100	100	100	100	100	50	55
Liquid product, wt %	97·07	83·9	61·61	53·64	31·81	9·22	2·76
Sp. gr. of liquid product	0·9147	0·9439	1·0160	..	..	..	..
Vol. of gas at NTP/100g. of feed, litres	1·266	14·10	28·91	38·87	54·58	83·99	89·76
Coke deposit (wt % on feed)	0·53	1·03	3·79	7·93	28·73	57·29	64·59
Analysis of liquid products, vol. %							
Saturates	29·1	9·2	Nil	Nil	Nil	..	..
Unsaturates	15·5	17·8	7·8	5·5	4·8	..	..
Aromatics	55·4	73·0	92·2	94·5	95·2	..	..
Gaseous products, vol. %							
CO_2	Nil	Nil	Nil	Nil	Nil	Nil	Nil
C_nH_m	41·5	44·9	49·6	32·7	5·0	3·0	1·3
CO	Nil	Nil	Nil	Nil	Nil	Nil	Nil
C_nH_{2n+2}	56·3	49·7	42·0	54·1	65·3	38·7	32·7
H_2	2·2	5·4	8·4	13·2	29·7	58·3	66·0

TABLE 3—COMPOSITION OF GASEOUS PRODUCTS FROM THERMAL CRACKING OF DIFFERENT FEEDS

	Light tar distillate (23·0% tar acids)			Light tar distillate (49% tar acids)			Pure tar acids		
Cracking temp., °C.	550	700	900	550	700	900	550	700	900
CO_2	1·4	0·5	0·4	0·9	0·2	1·1	1·4	1·1	6·5
C_nH_m	38·5	12·1	1·1	39·1	16·2	0·9	15·8	2·8	0·1
CO	3·0	6·6	4·6	4·8	13·3	8·2	15·0	20·3	14·7
H_2	6·7	29·3	71·4	10·0	36·1	69·9	18·8	45·3	65·3
C_nH_{2n+2}	50·4	51·5	21·5	45·0	40·2	19·9	49·0	30·5	13·4

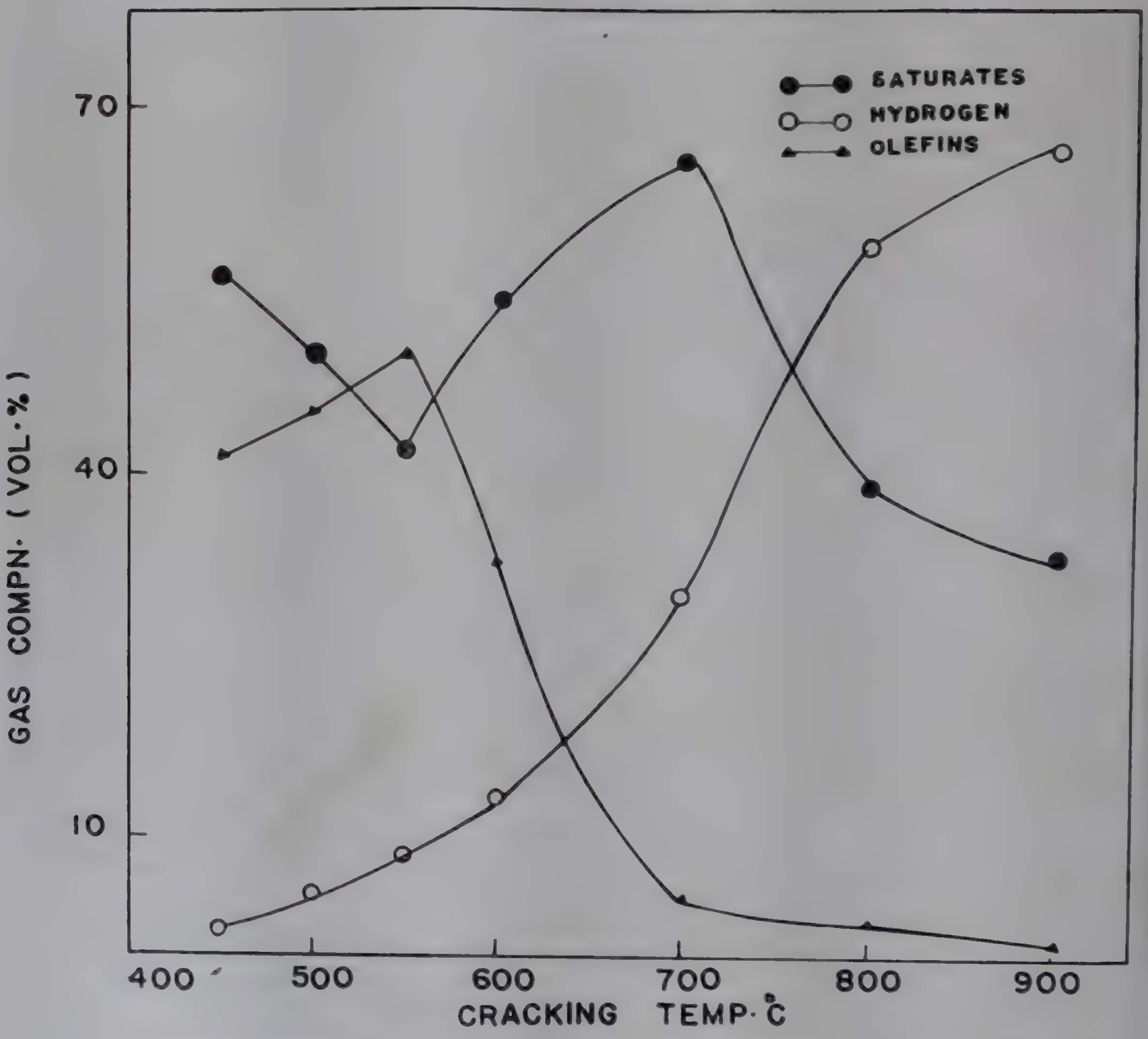

Fig. 2—Composition of gas at different cracking temperatures

saturates, olefins and aromatics. The results may be explained on the basis of Rossini's data[4] on the free energies of formation of different type hydrocarbons, the stability of which, for the given number of carbon atoms, increases in the order: paraffins, olefins, aromatics with large substituted groups, and unsubstituted aromatics and on the basis of the free energies of various reactions[5] which take place at the cracking temperatures. It is therefore, likely, that reactions of the type of splitting decomposition of paraffins and olefins to gaseous olefins may be predominant at temperatures of 450° to 550°C., thus giving higher percentages of olefins in gaseous products. As the temperature is raised, from 550° to 700°C., secondary reactions of unsaturates like, condensation to aromatics, decomposition to diolefins and paraffinic gases, etc. are possible to a greater extent giving less of unsaturates and more of saturates in the gaseous products. Further increase in temperature perhaps accelerates the secondary reactions of olefins, splitting docomposition of paraffins and substituted aromatics to methane and hydrogen and the elemental docomposition to coke and hydrogen.

Table 3 indicates the effect of thermal cracking of different feeds containing tar acids on the composition of gaseous products. With increasing tar acids content in the raw material, there is a definite suppression of the rise in saturates above 550°C. and in unsaturates between 500° and 550°C. Gas yields decreased with increasing tar acid content in the feed. Oxygenated compounds like tar acids in neutral oil would produce increased quantities of carbon monoxide in the gas with the rise in cracking temperature. Higher coke yields resulted with increasing tar acids content.

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New Processes for Effecting Chemical Reactions in Homogeneous Temperature Fields

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For the thermal decomposition of hydrocarbons and for effecting other chemical reactions a reaction chamber is used in which no installations are provided. The turbo gasifier has proved its worth in which a rotating impeller in the interior of the gasifying chamber influences the processes of flow and mixing functions. The mode of operation according to the new processes is described and the fields of application stated.

OIL CRACKING PROCESSES

The conversion of liquid or gaseous hydrocarbons into gases for heating or chemical processing plays at present an important role in industry and for town gas supply. Generation of producer gas, synthesis gas and town gas from oils as well as from natural gases is already known. The production of town gas by such processes has recently assumed increasing importance.

Gases are produced by decomposition or oxidation of hydrocarbons at temperatures between 700° and 900°C. The composition of the gas as a function of the decomposition temperature depends on the known chemical equilibrium conditions; the aim is to achieve the reaction temperature as close to the theoretical as possible.

In the present article the purely thermal decomposition in presence of oxidizing mediums (air or oxygen and steam) is dealt with. The reaction chamber is free from materials which catalytically influence the conversion. The gasifying and decomposition process is continuous, and all phenomena particularly mixing, temperature and reaction kinetics occurring in the reaction chamber must be controlled by uniform kinetic conditions.

The apparatus used was developed by Klöckner-Humboldt-Deutz A. G., in close cooperation with the Hermann-Fottinger-Institute of the Technical University of Berlin and with Messrs Farbenfabriken Bayer A. G., after considerable experimental work.

THERMAL DECOMPOSITION AND OXIDATION PROCESS

Lighter hydrocarbons in the form of permanent gases are produced by the thermal decomposition of hydrocarbons when reacted with oxygen (or air) and steam, carbon monoxide and carbon dioxide as well as small quantities of condensable aromatic hydrocarbons are formed and free carbon or soot in the case of incomplete gasification in the earlier processes. Nearly 50 per cent by weight of the carbon contained in the oil is converted into carbon dioxide and carbon monoxide through intermediate reactions whose nature is not known in detail; in this connection the completeness of the conversion to avoid carbon or soot formation represents one of the main problems in the gasification of liquid or gaseous hydrocarbons. Pesides, part of the hydrogen gets oxidized to water.

The gasification of carbon to carbon monoxide and carbon dioxide by means of pure oxygen or air is known. Every coal gas producer achieves this by gasifying solid fuels.

However, in the case of gasification of hydrocarbons, some special problems arise: Firstly, no free carbon or soot should be allowed to form. If this is not possible, the soot must be oxidized by a separate process, which means the gasification cannot be carried out continuously. Since the formation of carbon is a function of temperature, attempts have been made to solve this problem by controlling the temperature in the gasifier.

With all gasifying processes in which the reactant is sprayed in the gasifying medium the reactions occur according to the law of mass action. This means that the concentrations and thus the reaction velocity decrease in a measure depending on the extent of the reaction.

TURBO-GASIFIER

These two factors indicate that a gas producer in which aerosol type or gaseous hydrocarbons are to be converted into gas, a control of the thermal and mechanical parameters independent of the chemical process must be provided. A possible realization of this concept is represented in Fig. 1.

The turbo-gasifier is a gas producer or reactor in which pulverized coal, sprayed oil, gasoline or gaseous hydrocarbons are brought into reaction with oxygen in the form of air, enriched air, or pure oxygen in the presence of steam. The designation "turbo-gasifier" is given since a rotating impeller in the interior of the gasifying chamber influences the flow of gas

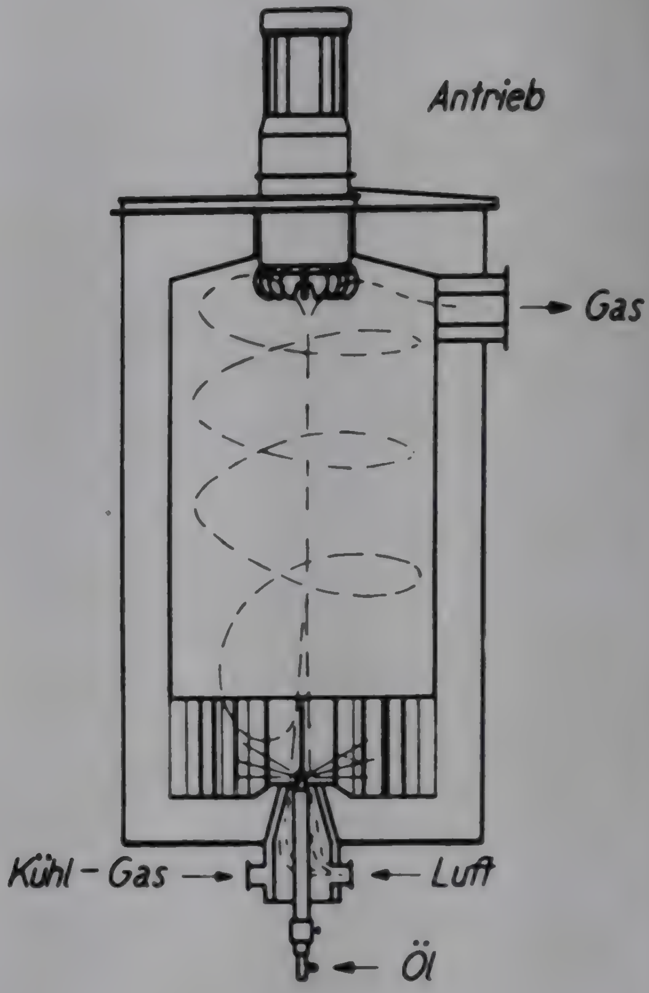

FIG. 1—TURBO-GASIFIER FOR OPERATION WITH LIQUID FUELS: Antrieb--driving mechanism; öl—oil; Kuhlgas—cooling gas; Luft—air

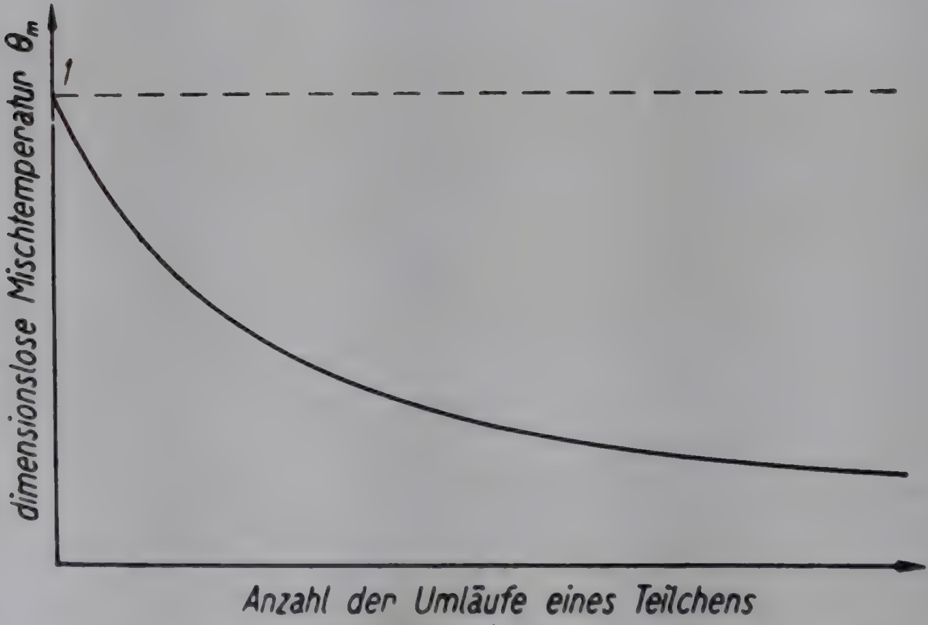

FIG. 2—EFFECT OF MECHANICAL MIXING ON TEMPERATURE: X-axis—Circulation No. of a particle; Y-axis—Mixing temperature (dimensionless)

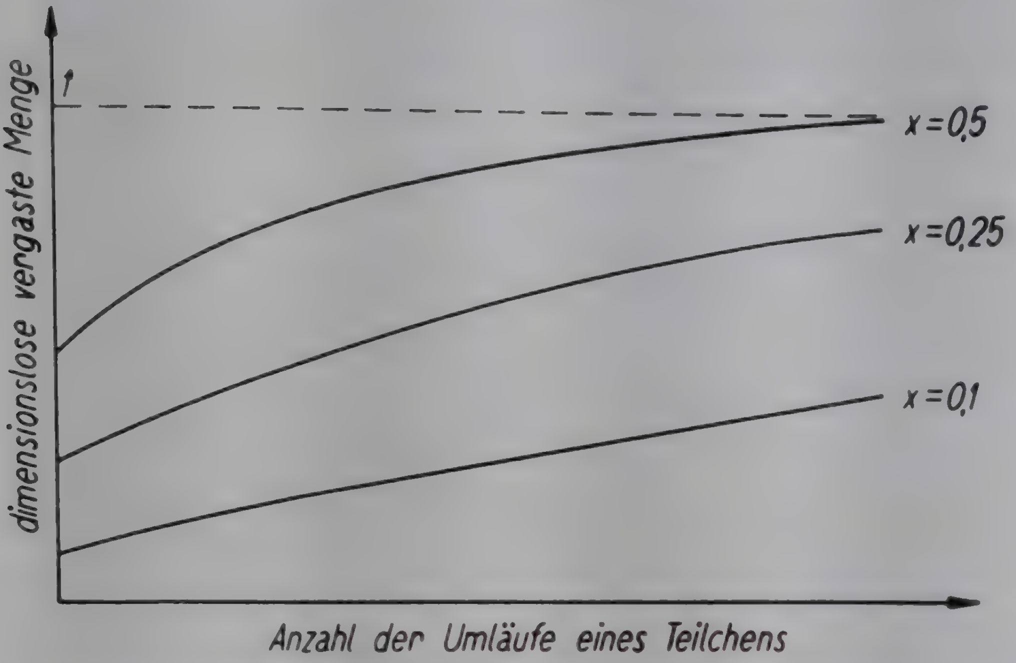

FIG. 3—GASIFICATION OF A PARTICLE IN THE TURBO-GASIFIER: X-axis—Circulation No. of a particle; Y-axis—Gasified quantity (dimensionless)

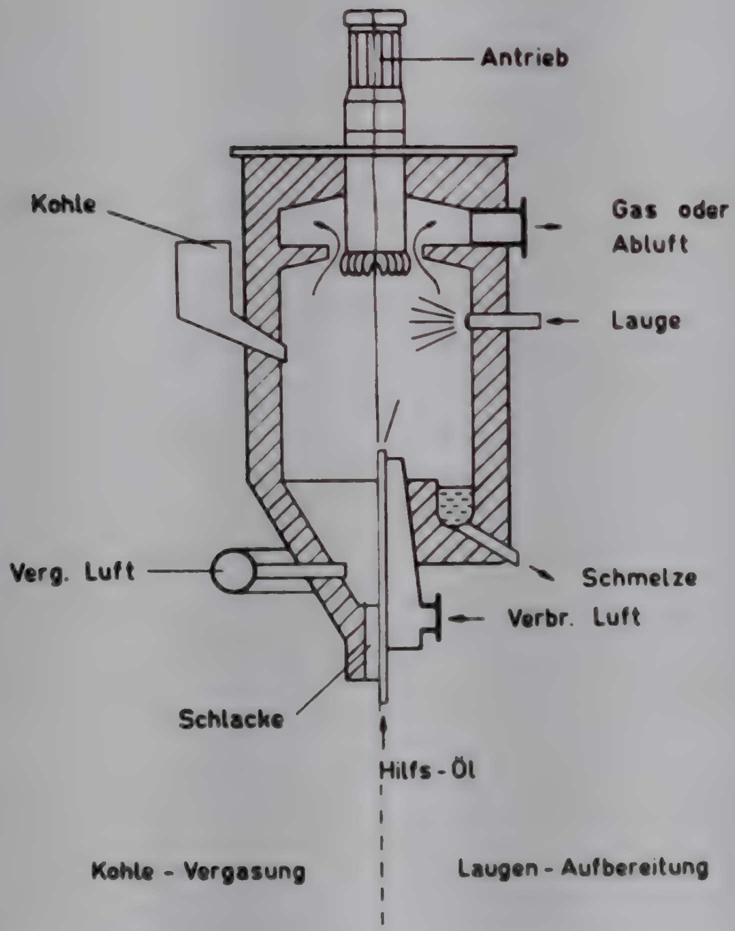
Antrieb
Kohle
Gas oder Abluft
Lauge
Verg. Luft
Schmelze
Verbr. Luft
Schlacke
Hilfs - Öl
Kohle - Vergasung
Laugen - Aufbereitung

FIG. 4—SECTIONS OF A COAL GAS PRODUCER AND AN APPARATUS FOR REGENERATION OF BLACK LIQUOR: Antrieb—Driving mechanism; Kohle—coal; Gas oder Abluft—gas or waste air; Lauge—Black salt; Verg. Luft—Gasification air; Schmelze—Fused salt; Schlacke—Slag; Hilfs-öl—Auxiliary fuel oil; Verbr. Luft—Combustion air; Kohle-Vergasung—Coal gasification; Laugen—Aufbereitung—Regeneration of black liquor

and air as well as the motivating and mixing actions of the sprayed hydrocarbons or of the pulverized coal.

Here the mechanical mixing motions are particularly important. It is not easy to describe the way the rotating impeller acts. Roughly speaking it may be said that a secondary motion is superimposed on the conveying stream of the gas through the producer. The flowing phase is turbulent. The eddies originating from the vanes of the impeller produce velocity fluctuations, which strongly support the mixing action.

Experiments had to be carried out to find proper shapes of the impeller and of the internal installations necessary to reach the required physically homogeneous mixture of aerosol, gas and air.

The effect of mechanical mixing on the temperature and gasification of aerosol may be described as follows:

The gasifying process is exothermic. The maximum heat generation takes place in the neighbourhood of the inlet opening for the aerosol, and in the case of oil gasification at the atomizing jet. With media at rest, the increasing temperature would be proportional to the ratio of the heat of reaction and gasifying air volume. Mechanical mixing actions produced by the impeller supply the air, which must also be heated up as ballast, to the primary reaction temperature. The increase in temperature $\triangle \mathrm{Tm}$ of the mixture is a function of the produced volume Q_1 and of the circulating volume Q_2 as well as of the initial temperature. Thus

$$\triangle \mathrm{Tm} \propto \frac{Q_1}{Q_1+Q_2} \propto \frac{1}{1+n}$$

where $n=Q_2/Q_1$. With increasing Q_2 the mixing temperature approaches an asymptote which represents constant initial temperature in the gasifier in the case of homogeneous mixture (Fig. 2).

The following relations are applicable in the case of perfect gasification.

It is plausible that the oxygen concentration reaches a maximum near the air inlet—in this case at the bottom of the producer. Recent tests have shown that there is still a considerable oxygen concentration in the eddy core which under certain circumstances reaches up to the impeller. On the other hand the oxygen in the gas behind the impeller decreases to fraction of a per cent by volume due to the turbulence near the vanes.

A particle undergoing gasification may pass through the gasifier executing one or more circuits. The number of circuits is assumed to be proportional to the ratio of Q_2/Q_1.

When the gasified portion after one pass through the producer is designated x, the gasified volume V increases in proportion to the original volume V_0 according to the equation:

$$V/V_0=1-(1-x)^{n+1}$$

Here x is a number smaller than 1 and indicates a percentage of the volume in this simplified case. These relations are shown in Fig. 3.

TABLE 1—ANALYSES OF GASES OBTAINED BY GASIFICATION AND CRACKING OF COAL AND VARIOUS HYDROCARBONS IN THE TURBO-GASIFIER

FUEL	GASIFYING MEDIUM	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	H_2	CO	CO_2	N_2	NET CALORIFIC VALUE kcal./Nm^3
Coal	Oxygen	..	..	..	..	..	..	..	..	98	2	..	2960
Light fuel oil	Air	6·4	0·2	2·6	0·2	0·6	..	..	5·4	16·4	3·7	64	1780
Heavy fuel oil	Air	6·1	0·2	2·0	0·2	0·4	..	..	4·5	17·2	4·7	65	1660
Butane	Air	7·8	..	3·4	0·3	0·1	..	..	4·8	12·0	4·0	68	1800
Butane	Air	8·9	..	5·5	0·7	1·5	1·8	..	3·6	10·4	3·0	..	2800
Light benzine	Air	7·9	0·3	5·1	0·5	0·9	0·3	..	2·8	14·6	3·2	63·5	2290
Light benzine	Oxygen	22·6	0·5	21·0	2·6	9·5	0·5	1·4	7·4	19	6·2	7·8	8460

APPLICATIONS

The process described here besides being applied to the decomposi
of liquid or gaseous hydrocarbons for producing gas for heating and chemic
processing has also been used for the production of gas from coal fi
and for the regeneration of the so-called black liquors from cellulose (pul
factories applying the sulphate process. Fig. 4 shows a sketch of the un
used in the case of the latter two applications.

In Fig. 4, the left half shows the section of a coal gas producer a
the right half that of an apparatus for regenerating black liquor from t
sulphate process. A common feature is a water-cooled impeller at the t
of the producer, which runs at high speed, produces an eddy current i
the centrifugal field, of which non-gasified carbons or slags are separat
from the gas as in the case of a cyclone. In the gas producer gasificatio
cracking and oxidation reactions take place. In the case of the regenerati
of the black liquor, carbon monoxide is generated from the fuel oil a
the organic constituents of the black liquor. It is most essential that t
alkaline constituents of the liquor are chemically converted, e.g. sodiu
sulphate must be reduced to sodium sulphide at reaction temperatu
between 900–1100°C.

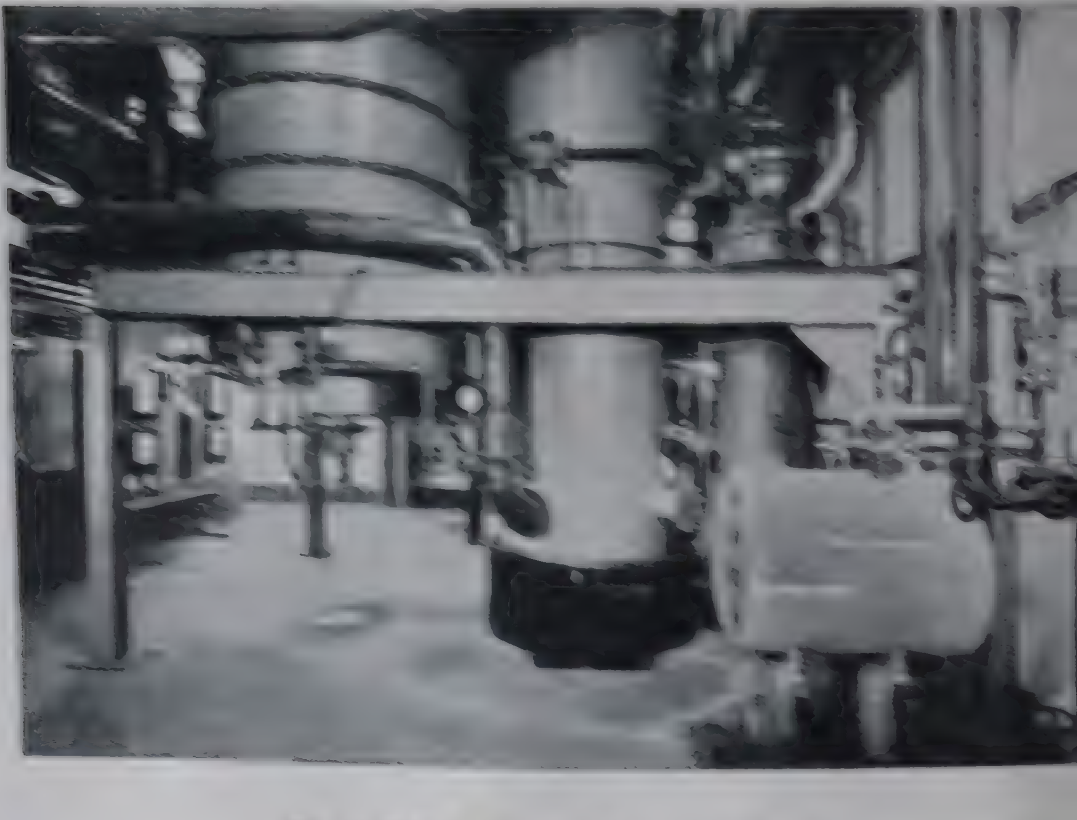

Fig. 5.—View of an [illegible] plant

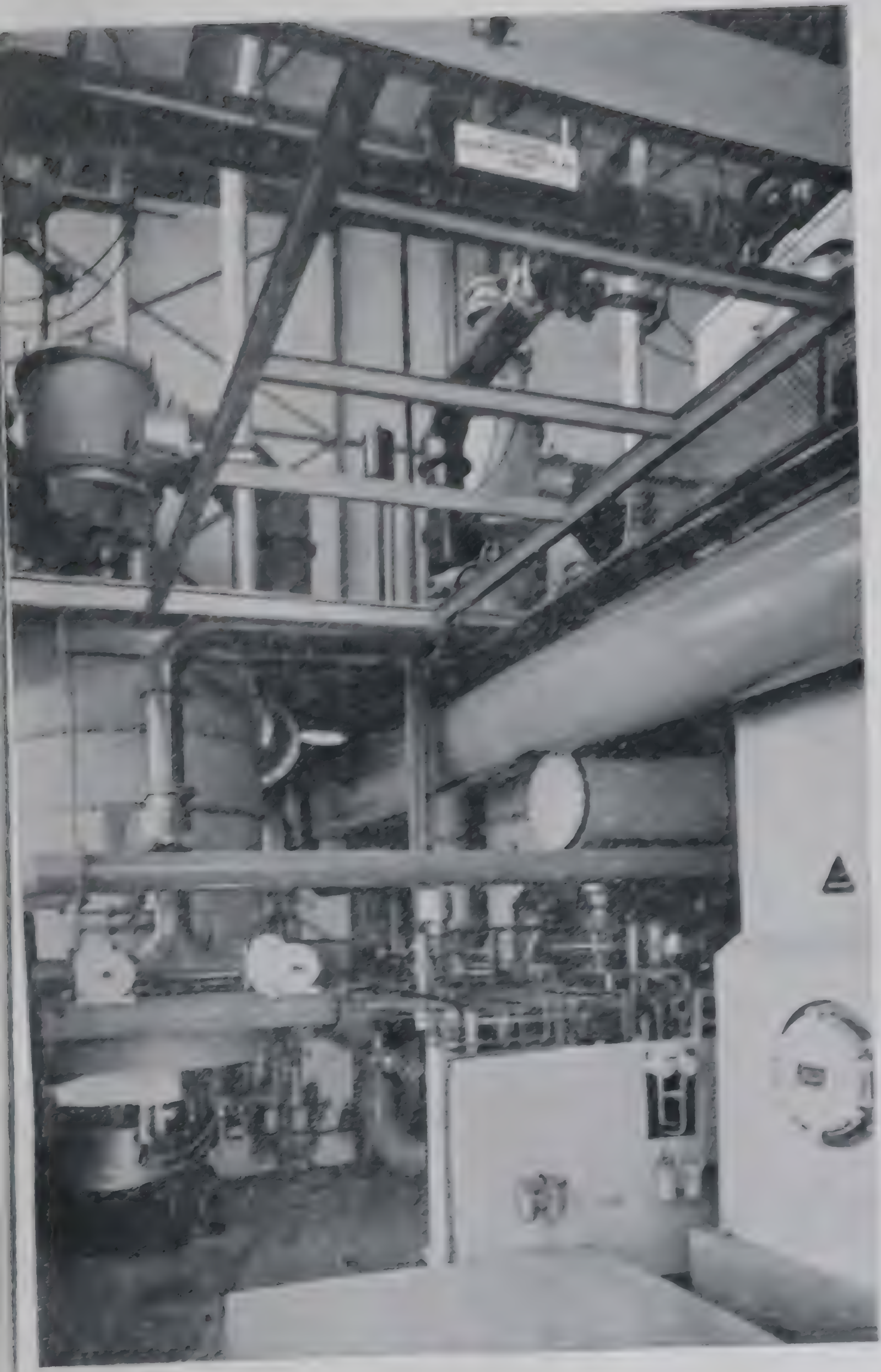

FIG. [illegible]—VIEW [illegible] OF THE [illegible] PLANT

During this process the water is evaporated and the organic constituents of the liquor are burnt to a gas containing both carbon monoxide and carbon dioxide. The product is continuously discharged from the reactor as fused salt. The produced gases can be adjusted to any desired calorific value between 0-1000 kcal./Nm^3. Practically speaking, they are free from salt, so that their chemically bonded and sensible heat can be used for air preheating or steam raising without any danger of fouling the contact surfaces of the heat exchanger. The degree of reduction, i.e. the sulphide portion, referred to the sum of sulphides and sulphates amounts to 85-90 per cent.

Figs. 5 and 6 show the views of an oil gasifying plant. Table 1 gives the analyses of the gases produced in the turbo-gasifier.

Technique of Counter-current Distribution and Systematic Study of Homologues and Isomers

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Results of counter-current distribution studies on the separation of phenols from low temperature tars are reported. The following solvent pairs: (i) cyclohexane—0·1 per cent aqueous sodium chloride solution, (ii) cyclohexane—aqueous sodium metasilicate solution, (iii) cyclohexane with butanol-water (with and without sodium chloride) were found suitable for low boiling monohydrics, high boiling monohydrics and polyhydrics respectively. The concept of band spread in counter-current distribution can be used for proper fractionation and for predicting the separation of multicomponent mixtures of phenols.

The technique of counter-current distribution (C.C.D.) discovered by Craig in 1944 is an analytical tool of immense fractionating power and highly suitable for detection, separation and estimation of complex mixtures covering almost all branches of organic chemistry. The C.C.D. technique has already been applied to the classes of compounds mentioned in Table 1. C.C.D. is a batch multiple extraction unit operating on the principle of partition coefficients of solutes between a properly chosen pair of immiscible solvents. Usually the heavier solvent is kept fixed while the lighter solvent is transferred from one cell to another after each cycle of equilibration, stratification, and decantation of phases. Unlike other fractionation processes like distillation and chromatography, accurate prediction of the complete course of separation is possible in C.C.D. So long the chief disadvantage of C.C.D. has been the labour involved in the application of large transfers. But this limitation has now been overcome by the development of a fully automatic equipment capable of 1000 transfers or even

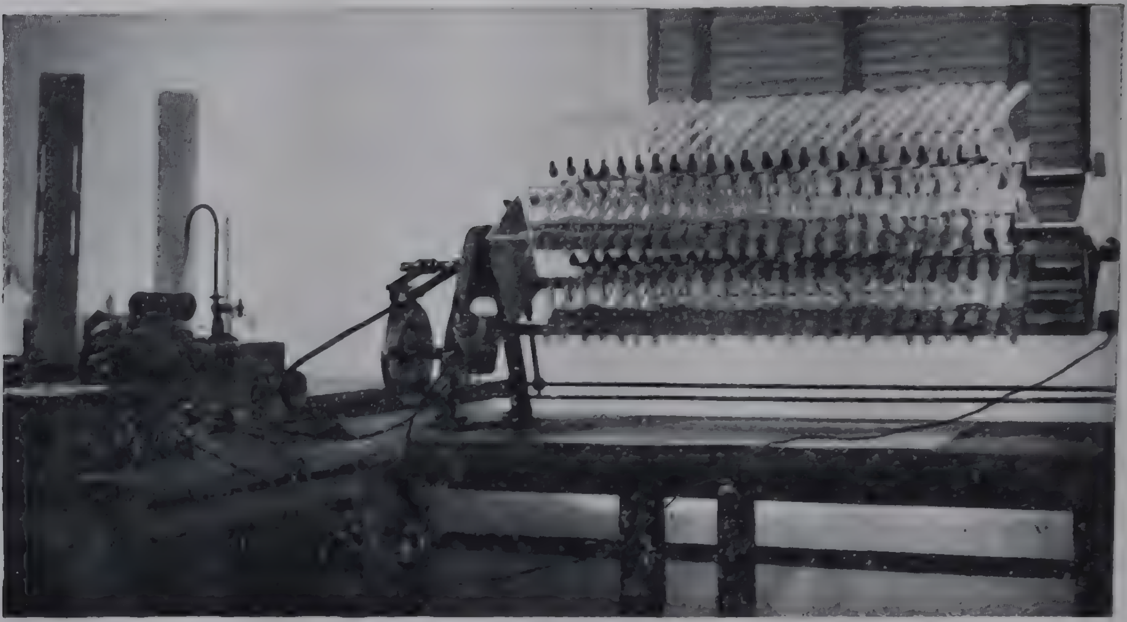

Fig. 1—C.C.D. unit of 50 tubes

TABLE 1—TYPES OF COMPOUNDS STUDIED BY C. C. D. TECHNIQUE

Fatty acids
Fats and oils
Amino acids
Aromatic acids
Phenols[2,3]
Aromatic hydrocarbons[4]
Polypeptides
Aminomethyl vinyl ethers[5]
Antibiotics
Penicillins
Xanthomycins
Aromatic amines
Heterocyclic bases
Antimalarial bases
Alkaloids
Polynuclear hydrocarbons
Nucleotides
Vitamins
Biotin
Hormones
High polymers
Rare earths[6]

Reference for the rest of the compounds is (7).

more. A C.C.D. unit of 50 tubes assembled in the C.F.R.I. is shown in Fig. 1. The theory, principle, and mode of operation of C.C.D. have been exhaustively reviewed by Craig[7]. Craig's C.C.D. technique which works on a single feed is, however, not suitable for commercial exploitation. Attempts have been made recently to modify the Craig's apparatus with provision for simultaneous movement of both the phases in actual counter-current directions and with continuous feeding of large samples at predetermined stages, and continuous recovery of the separated components at both ends of the apparatus. Such a modification has actually been employed in the large-scale separation of space-age metals[6]. Theory of this new model has been extensively discussed by Barker and Beecham[8]. C.C.D. technique is now being widely used in U.S.A., Germany, Australia, and in many atomic energy establishments.

SELECTION OF SOLVENT PAIR

Selection of solvent pair for a particular type of compounds is most important in C.C.D. In the solvent pair employed, all the components in the sample must behave 'ideally'. A solute is said to behave ideally when it obeys equation (1)[1-9] for fundamental procedure and equation (2)[10] for single withdrawal procedure. Equations (1) and (2) have also been utilized: (*i*) for simple interpretation of fundamental and withdrawal procedures, (*ii*) for comparing the theoretical and observed distribution curves, (*iii*) for resolving the composite distribution curves into individual components, (*iv*) for accurate determination of partition coefficient of a solute, and (*v*) for exact location of tube/withdrawal containing the maximum amount of solute.

Monohydric Phenol. It has been found in the C.F.R.I. that cyclohexane—0·1 per cent aqueous sodium chloride is a suitable solvent pair for the lower phenols, because about 40 available pure phenols have been found to give linear plot of equation (1) (Fig. 2).

For the C.C.D. analysis of higher phenols the problem was to make them soluble in water by the incorporation of a suitable additive. Sodium metasilicate was found to be a suitable additive. Plot of T_r/T_{r+1} against $r+1/n-r$ (Fig. 3) proves that higher phenols behave 'ideally' in the solvent pair cyclohexane—aqueous metasilicate.

Polyhydric Phenols. C.C.D. technique has not yet been employed for the polyhydric phenols. The two solvent pairs mentioned above for

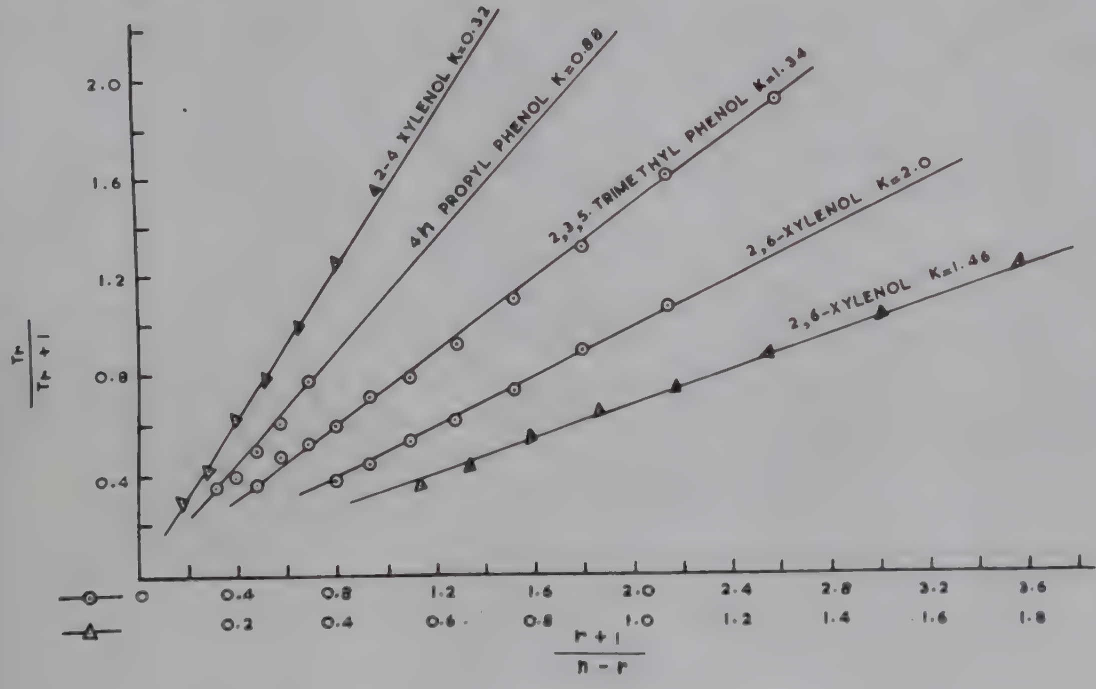

FIG. 2—PLOT OF EQUATION (1) FOR LOWER PHENOLS

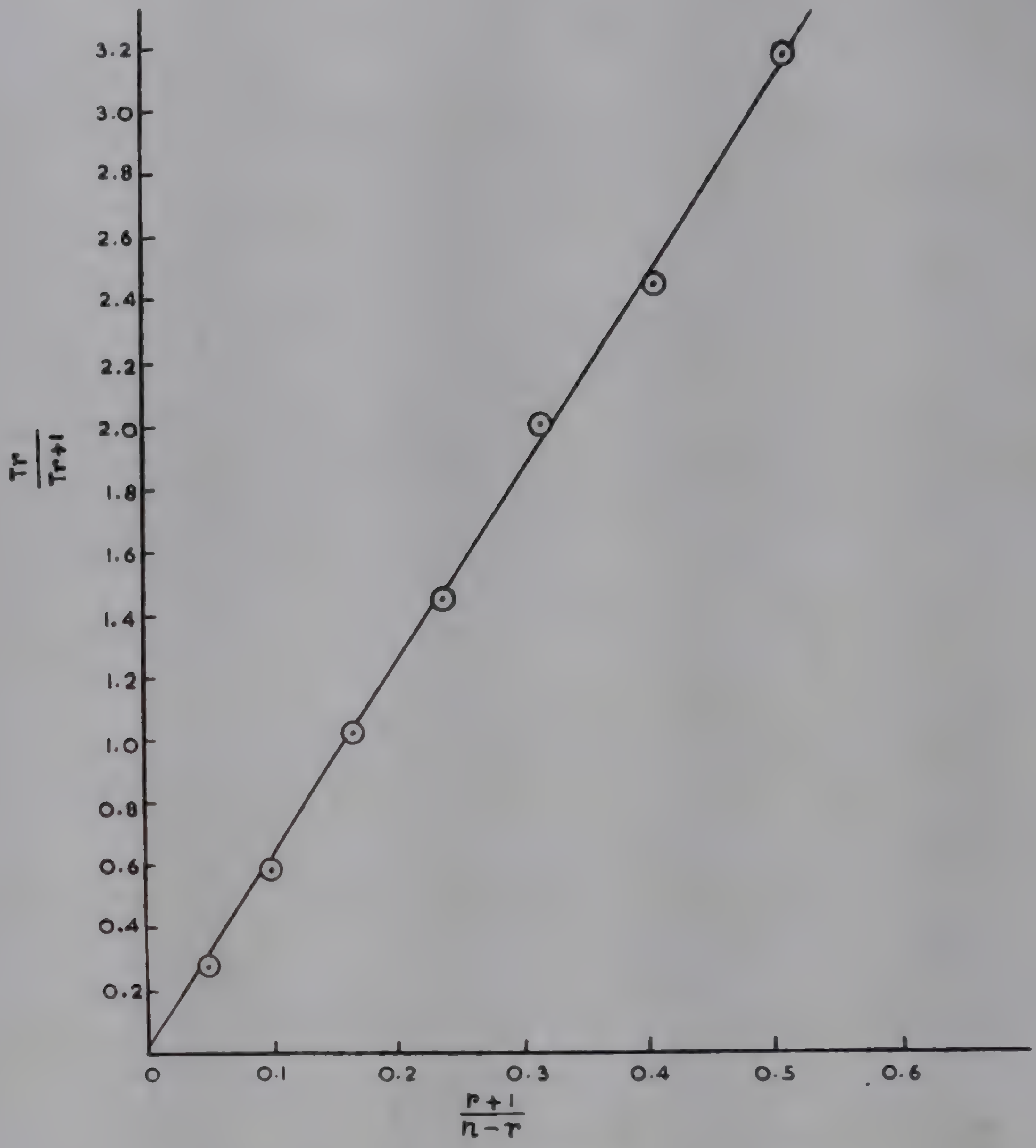

Fig. 3—Plot of equation (1) for higher phenols

monohydric phenols are, however, not suitable for polyhydric phenols. Using cyclohexane as the mobile solvent, attempt was made with as high as 10 per cent concentration of sodium chloride in water (in order to suppress the high solubility of polyhydric phenols in water), but without success. It was observed with dihydric phenols that their partition coefficients between butanol and water are very high, thereby indicating that butanol is a much stronger solvent than water for the polyhydric phenols. Cyclohexane containing butanol and water with or without sodium chloride was, therefore, considered suitable for polyhydric phenols. Plot of equation (1) for 4-methyl catechol between 0·1 per cent sodium chloride and 5 per cent (vol.) butanol in cyclohexane shows ideal behaviour for the solute whose

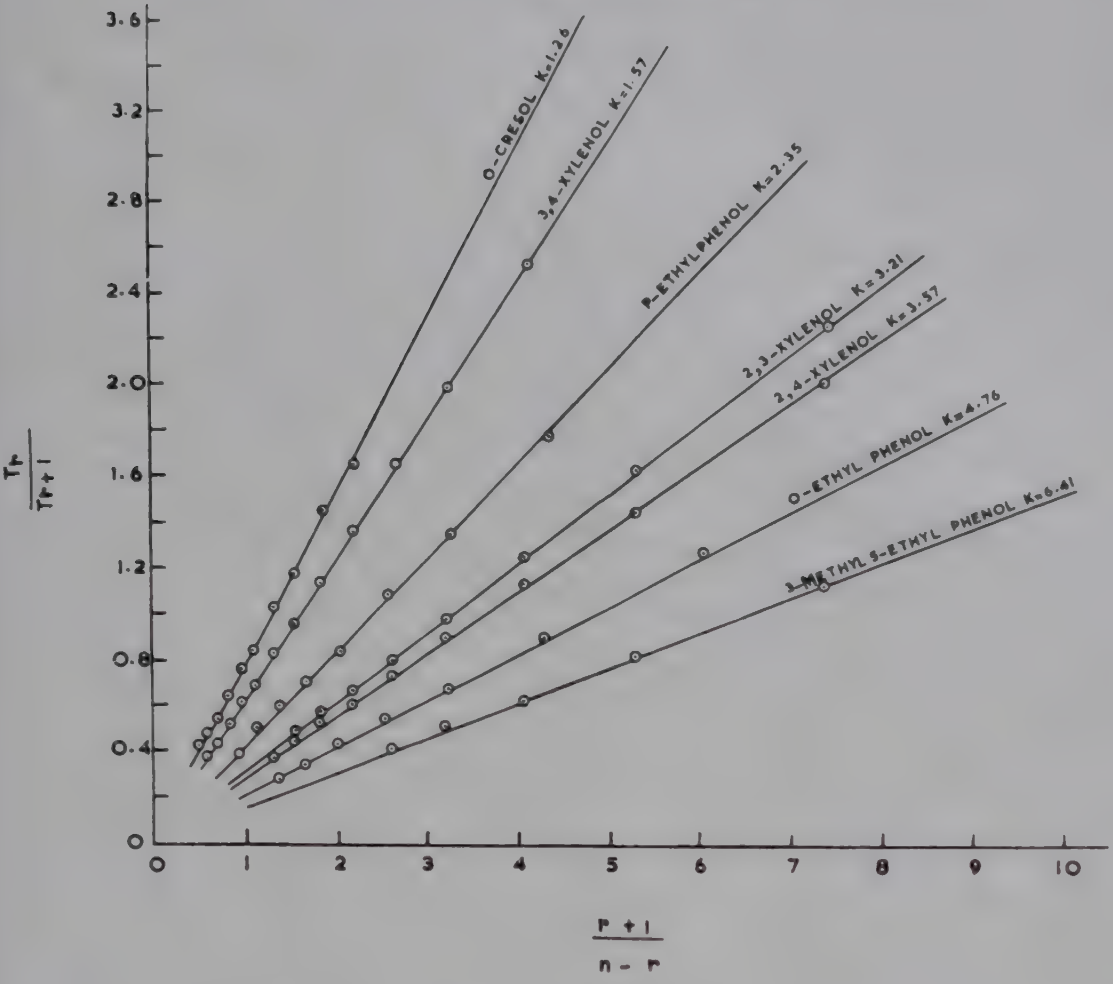

FIG. 4—PLOT OF EQUATION (1) FOR POLYHYDRIC PHENOLS

partition coefficient is 0·164 (Fig. 4). Increase in the strength of butanol in cyclohexane will invariably increase the partition coefficients of polyhydric phenols. Therefore, cyclohexane containing proper amount of butanol and 0·1 per cent sodium chloride is considered a suitable solvent pair for polyhydric phenols.

PRE-REQUISITES FOR SYSTEMATIC STUDY

After the selection of a suitable solvent pair, it is required for systematic investigation of homologues and isomers (such as the phenols in tars from low temperature carbonization of coals) to know the correlations between their structures and partition coefficients in order to employ the most suitable transfer number for proper resolution, identification and estimation of all the components in a sample.

It is clear from the theory of C.C.D.[7] that partition coefficient is the only parameter in C.C.D. fractionation. It has been established in this laboratory that the concept of 'band spreads' for solutes of known partition coefficient is the most vital aspect of C.C.D. fractionation. Band spread[11] of a solute has been shown to be given by equation (3) for fundamental procedure and equation (4) for withdrawal procedure.

EQUATIONS AND THEIR NOMENCLATURES

$$\frac{Tr}{Tr+1}=\frac{1}{K}\times\frac{r+1}{n-r} \tag{1}$$

$$\frac{Tr+1}{Tr}=\frac{1}{K+1}\times\frac{u+r+1}{r+1} \tag{2}$$

$$S=\frac{6{\cdot}07\sqrt{n}\;\sqrt{K}}{K+1} \tag{3}$$

$$S=\frac{6{\cdot}07\sqrt{K+1}\;\sqrt{u}}{K} \tag{4}$$

where T_r = fractional amount of solute in the rth tube

K = partition coefficient of the solute

n = transfer number employed in the fundamental procedure

u = tube number from which withdrawals are collected

S = 'band spread' of a solute.

COMPLETE INVESTIGATION OF PHENOLS IN TARS FROM LOW TEMPERATURE CARBONIZATION OF COALS

Factors like size, shape and nature of substituents as well as the nature of aromatic nucleus which determine the partition coefficient of phenols in solvent pairs like those mentioned above have been investigated by the C.F.R.I.[12] Now it is possible not only to judge whether one isomer of phenol will have a lower or higher partition coefficient than another, but also to predict nearly quantitatively its partition coefficient from the structure. The logarithm of the partition coefficient of homologues and isomers of phenols when plotted against the number of carbon atoms inside chains, is found to give straight lines.

Now, for C.C.D. study of tar acids the only problem is to select transfer number of proper resolution of all the components in a mixture. This can be illustrated with a sample containing 10 phenols boiling between 178° and 210°C. Partition coefficients of these phenols actually determined between cyclohexane and 0·1 per cent sodium chloride together with their band spreads have been given in Table 2. Transfer number for the "desired separation" of a given sample has been defined as the one which will give five consecutive tubes (preferably near the peak concentration) containing one, two, or at the most, three solutes. From the concept of band spreads it can be shown that "desired separation" for the above mixture will be achieved by an application of 300 transfers fundamental procedure in an apparatus of 201 tubes (one such type is under construction in the C.F.R.I.). In this hypothetical analysis there are as many as three selection containing three solutes, which can, however, be easily resolved from optical densities at two suitable wave lengths and from the composite distribution curves.

The additional transfers above 200 were obtained, by reusing the first 118 tubes after $n=200$, in the second stage of operation for $n=300$.

According to the above principles lower phenols in low temperature tars have been determined by 80 transfers C.C.D. between cyclohexane and 0·1 per cent aqueous sodium chloride in the 50-tube apparatus[9]. The 68-95°C. (at 10 mm. Hg) fraction of purified mixed tar acids in tars obtained from coal carbonized at 650°C. in Swoboda electric oven (Sample A) and coal carbonized at 550°C. in Fischer assay apparatus (Sample B) consisted of 6·2 per cent phenol, 5·2 per cent *m*-cresol, 6·3 per cent *p*-cresol and 7·0 per cent *o*-cresol in Sample A, and 4·6, 4·1, 5·8 and 6·1 per cent in Sample B respectively.

TABLE 2—C.C.D. FRACTIONATION SCHEME OF TEN LOW BOILING PHENOLS (178–210°C.) BY 300 TRANSFERS FUNDAMENTAL PROCEDURE IN 210-TUBE APPARATUS

COMPOUND	K	BAND SPREAD FOR n=200			BAND SPREAD FOR n=300			TUBES FOR ANALYSIS	COMPONENTS PRESENT
		r_b	r_m	r_e	r_b	r_m	r_e		
Phenol (a)	0·17	14	29	43				27 to 31	(a)
m-Cresol (b)	0·625	56	77	97				75 to 80	(b) and (c)
p-Cresol (c)	0·645	57	78	98					
o-Cresol (d)	1·25	90	111	132		167	192	109 to 113	(d)
m-Ethylphenol (e)	2·27	119	139	158	184	208	231	208 to 212	(e) and (f)
p-Ethylphenol (f)	2·33	121	140	159	186	210	233		
2-4-Xylenol (g)	3·65	140	157	174	215	236	257		
2-5-Xylenol (h)	3·70	141	158	175	215	236	256	234 to 240	(g), (h) and (c)
o-Ethylphenol (i)	4·75	150	166	182	228	248	267	258 to 261	(i) and (j)
2-6-Xylenol (j)	8·30	166	179	192	252	268	284	268 to 272	(j)

r_b =tube where the distribution band begins.
r_e =tube where the distribution band ends.
r_m =tube which contains the maximum amount of solute.

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Gas Chromatography of Coal Tar Phenols

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Gas liquid partition chromatography (G.L.P.C.) offers a quick and reliable method for the resolution of most of the coal tar phenols. This paper reviews the work on G.L.P.C. of phenols by various workers. The role of selective stationary phases in gas chromatography is briefly discussed.

The relative retention times of phenols (b.p. up to 220 C.) are determined on a tricresyl phosphate (technical) stationary phase with and without the addition of orthophosphoric acid. The results indicate that presence of ortho-substituent/s, e.g. alkyl-, alkoxy-, in the phenol decreases the retention time as compared to the presence of meta, and/or para-substituent/s. This effect becomes more pronounced when both the positions, ortho- to phenolic group are occupied.

Coal tar and aqueous ammonical liquors, specially from low temperature carbonization (l.t.c.) plants are rich, both in mono- and polyhydric phenols, usually known as tar acids. The complex nature of these tar acids and also the close boiling nature of some of these phenols pose difficult problems in identification, separation and estimation of the constituents. The conventional fractional distillation followed by chemical and spectroscopic estimation is mostly limited to low boiling tar acids (up to xylenols). The quantitative results obtained from these are also not satisfactory. Chromatographic and counter-current distribution techniques developed in recent years offer a solution to a better study of the tar acid components. Among the chromatographic methods, gas chromatography being superior and simpler offers a rapid and reliable method of separation.

The principles involved in gas chromatographic technique and the equipment required have been described in literature[1-4].

REVIEW OF WORK DONE ON GAS-LIQUID PARTITION CHROMATOGRAPHY (G.L.P.C.) OF PHENOLS

It was early in 1958 that Irvine and Mitchell[5] published their work on G.L.P.C. of some 30 phenols (boiling up to 250°C.) commonly occurring in coal tar. Apiezon-L grease (about 30 per cent W/W on Celite 535) served as the stationary phase, nitrogen as the carrier gas and a thermal conductivity cell as the detector. The retention times at temperatures of 135, 155, and 183°C. were reported. Typical data obtained by these workers at 183°C. at which temperature alone sharp peaks were obtained, are shown in Table 1. They achieved separation only to a limited extent; close-boiling phenols, e.g. *m*-, and *p*-cresols, 2, 5- and 2,4- xylenols, etc. did not separate. Later, the same authors[6] applied this method for the separation of the phenols occurring in tars from l.t.c. in a fluidized bed and collected various cuts using a fraction collector. The retention time data coupled with examination of these cuts by infrared spectroscopy, led to the identification of most of the phenols boiling up to 230°C.

Fitzgerald[7,8] recorded the retention times of 50 phenols on G.L.P.C. Using a combination of a non-polar (Apiezon-L grease) and a polar stationary phase (sodium salt of dodecylbenzene sulfonate), he examined the composition of low boiling phenols from Lurgi brown coal tar. A column length 24 ft (7/8 in. diam.) and a column temperature of 200°C. was employed for separation using nitrogen as carrier gas. Close-boiling phenols like *m*/*p*-cresols, 2,5- and 2,4-xylenols could not, however, be separated. He observed that methylated phenols did not separate well on the above stationary phases; however, he opined that chlorinated and dihydric phenols may separate well.

Di-*n*-octyl phthalate was used as stationary phase by Karr and coworkers[9], for determining the composition of phenols (boiling up to 234°C.) from l.t. tars of bituminous coal. The data on the estimation of phenols by G.L.P.C. compared well with those obtained by the conventional fractional distillation followed by infrared spectroscopy of various fractions. Some of the fractions which did not separate well on G.L.P.C. were collected and analysed by micro-infrared method. The relative retention times and other conditions used by them are given in Table 1. The two phenols, *o*-ethyl phenol and 2,4,6-trimethylphenol which could not be analysed by infrared owing to the low concentrations in their respective distillate fractions, could be readily identified and analysed by G.L.P.C.

Among the single stationary phases capable of separating close boiling isomers, the use of phosphoric esters of the phenols was reported by Paterson[10] and Brooks[11]. Paterson could separate only *m*/*p*-cresols on a 4-metre column using mixtures of tri-*o*-cresyl phosphate and phosphoric acid (5 : 5 or 5 : 3) as stationary phases. Brooks, on the other hand, separated all the close boiling isomers (up to about 220°C.) using 2,4-xylenol phosphoric ester as

TABLE 1—RELATIVE RETENTION TIME OF PHENOLS

(Phenol = 1)

[I—represents Apiezon-L grease (30% w/w on celite); Column length: 4 ft; Flowrate: 11 cc./min. Inlet pressure, 217 mm.; Outlet pressure, 58 mm.; Detector: Thermal conductivity type. II—represents Di-*n*-Octyl Phthalate (34·7% w/w on firebrick); Column length: 4 metres; Flowrate: 127 cc./min.; Inlet pressure 15 psig; Outlet pressure: Atmospheric; Detector: Thermal conductivity type. III—represents Di-*n*-Octyl sebacate (15% w/w on "Embacel"); Column length: 8 ft Flowrate: 25-30 cc./min.; Inlet pressure, 15 psig; Outlet pressure, atmospheric; Detector: Hydrogen flame type]

NAME OF PHENOL	B.P.* °C./760 mm.	I(a) (180°C.)	II(b) (160°C.)	III(c)
Phenol	181·8	1·0	1·0	1·0
o-Cresol	191·0	1·95	1·37	1·24
p-Cresol	201·9	2·1	1·70	1·49
m-Cresol	202·2	1·9	1·70	1·49
2 : 6 Xylenol	201·0	2·9	1·48	1·43
2 : 5 Xylenol	210·0	3·5	2·20	1·84
2 : 4 Xylenol	210·0	3·6	2·20	1·84
2 : 3 Xylenol	218·0	4·2	2·70	2·20
3 : 5 Xylenol	221·5	3·8	2·86	2·26
3 : 4 Xylenol	225·0	4·5	3·28	2·55
o-Ethyl Phenol	207·0	..	2·0	1·75
m-Ethyl Phenol	214·0	3·5	..	2·26
p-Ethyl Phenol	219·0	..	2·70	2·20
o-Isopropyl Phenol	211·0*	..	..	..
o-n-Propyl Phenol	220·5	..	2·86	..
p-Isopropyl Phenol	223·5	5·2	..	..
m-n-Propyl Phenol	228·0	6·1	..	..
p-n-Propyl Phenol	230·32	5·8	..	..
p-Isopropyl Phenol	229	5·2	..	..
4-Ethyl-2-methyl Phenol	224·5	5·6	3·46	..
3-Ethyl-2-methyl Phenol	227·0	6·7	..	..
5-Ethyl-2-methyl Phenol	223·0	6·0	..	..
5-Ethyl-3-methyl Phenol	234·5	6·3	4·42	..
2 : 4 : 6 Trimethyl Phenol	220·0	..	2·45	..
2 : 3 : 5 Trimethyl Phenol	230·1	7·0	4·42	..
2-Methyl-5-isopropyl Phenol	..	7·4	..	..
3-Ethyl-4-methyl Phenol	240·0	7·4	..	..
Indan-4-ol	244	9·4	..	..
3 : 5 Diethyl Phenol	239	9·1	..	..
4-n-Butyl Phenol	248	9·6	..	..
3 : 4 : 5 Trimethyl Phenol	248·9	9·6	..	..
2-Methylindan-4-ol	250	11·8	..	..
1-methylindan-4-ol	250	12·4	..	..
5-Methylindan-4-ol	250	14·2	..	..
6-Methylindan-4-ol	250	16·0	..	..

*As reported in Coal Tar Data Book.

(a) Irvine and Mitchell, (b) Karr (Jr) and coworkers, (c) Payn.

TABLE 2—RELATIVE RETENTION VOLUME DATA OF PHENOL ETHERS

(Reported by various workers)

Phenols	Apiezon M (a) 145°C.	*N*-Decyl phthalate (b) 150°C.	D. C. silicone oil (c) 125°C.	Di-n-butyl tetrachlorophthalate, 125°C.
	Relative to anisole=1		Relative to silyl ether of phenol=1	
Phenol	1	1·39	1·0	1·0
o-Cresol	1·56	2·05	1·59	1·68
m-Cresol	1·67	2·39	1·71	1·75
p-Cresol	1·67	2·43	1·84	1·89
o-Ethyl Phenol	..	2·23	2·36	2·34
m-Ethyl Phenol	..	3·89	2·80	2·81
p-Ethyl Phenol	..	4·03	3·05	3·10
2, 3-Xylenol	2·96	4·35	3·30	3·75
2, 4-Xylenol	2·42	..	2·77	3·01
2, 5-Xylenol	2·50	3·38	2·48	2·69
2, 6-Xylenol	2·05	2·14	3·06	3·55
3, 4-Xylenol	3·16	5·30	3·61	3·89
3, 5-Xylenol	2·50	4·32	2·86	2·85
2, 4, 6-Trimethylphenol	..	..	5·33	6·07
Guaiacol	2·51	..	3·23	3·48

(a) Work of Carruthers and coworkers, as methyl ethers.
(b) Work of Bergman and coworkers, as ethyl ethers.
(c) Work of Langer and coworkers, as silyl ethers.

stationary phase. He contradicted the earlier statement of Paterson that only a mixture of tri-*ortho*-cresyl phosphate and phosphoric acid in a particular proportion was able to separate the *m*/*p*-cresols and reported that the ester alone was an effective stationary phase for this separation. He investigated the suitability of phosphoric esters of various phenols as stationary phases for the separation of close-boiling isomers of phenols. The phosphoric esters of the following phenols are effective in separation (arranged in the decreasing order of their effectiveness), viz. 2,4-xylenol; 2,4-xylenol+2,6-xylenol (1 : 1); *o*-cresol; *o*-ethyl phenol; *m*-cresol; *p*-cresol; 2,5-xylenol; 3,5-xylenol; *p*-isopropyl phenol; ortho-*sec*-butyl phenol; 2-methyl-4-*ter*-butyl phenol.

Payn[12] reported the use of di-*n*-octyl sebacate as stationary phase for routine analysis of refined xylenols in actual plant control. The relative retention times as reported by him are also presented in Table 1.

The conversion of phenols into their ethers, viz. methyl-, ethyl-, etc. to reduce their boiling points and thereby to separate them at lower temperatures on G.L.P.C. is another approach to the analysis of phenols. Carruthers[13] and Bergman[14] reported the retention times of methyl- and ethyl ethers of phenols and the data are presented in Table 2. From their results, it is evident that close-boiling isomers did not separate. Langer[15] further improved the separation of phenol ethers by converting the phenols into their silyl ethers[16]. The relative retention times are presented in Table 2. Good separation of all the close-boiling isomers (boiling up to 220°C.) is reported.

With the stationary phases referred to above, separation of phenols or their ethers in most of the cases was according to their boiling points. Other stationary phases (designated as selective stationary phases), capable of separating components of close-boiling mixtures, taking advantage of the differences in the properties of one or more of the components to associate or form a hydrogen bond, etc. are coming into use in G.L.P.C. Inspite of the introduction of high efficiency capillary columns, the use of selective stationary phases is still gaining ground because of various other advantages.

Choice of a selective stationary phase for the separation of a particular mixture cannot be precisely predicted from the present knowledge of the theories on solubility. However, according to Keulmans[1], qualitative basis can be arrived at for solving a specific problem based on the knowledge of the following five classes of compounds to which the solute or the solvent may belong:

(1) The molecules form a three-dimensional net work of hydrogen bonds, e.g. polyalcohols, aminoalcohols, etc.
(2) the molecules possess active hydrogen atoms as well as electronegative atoms with free pairs of electrons (O, N, F), e.g. alcohols, phenols, fatty acids, etc.
(3) the molecules possess electronegative atoms, but no active hydrogen, e.g. ethers, ketones, esters, etc.
(4) the molecules possess active hydrogen atoms and negligible dipoles, e.g. aromatic and olefinic hydrocarbons, etc., and
(5) molecules without functional groups, e.g. saturated hydrocarbons, carbon disulphide, etc.

The above classification does not explicitly take into account the effects of mutual polarizability, formation of chemical bonds through the formation of loose adducts and of certain solutes which are more powerfully retained by the stationary phase if the classes to which they belong are close together.

Janak and coworkers[17,18] were the first to report studies on the influence of hydrogen bonding between hydroxyl groups of phenols and the functional groups such as—SH, NH_2 and—OH of the stationary phases on the separation of phenol and its homologues. Comparative data on relative retention times on the above-mentioned stationary phases are mentioned in Table 3. The degree of hydrogen bond formation between the phenolic hydroxyl and the functional group of the stationary phase is largely determined by the steric effects of substituents on the former. The phenols can thus be classified as (1) hydroxyl group is sterically free, e.g. phenol, *m/p*-cresols, 3, 5-xylenols, etc. (2) the hydroxyl group is hindered by substitution in the 2-position, e.g. *o*-cresol, 2, 5-xylenol, etc. (3) the hydroxyl group is blocked by the substituent in both 2- and 6-positions, e.g. 2, 6-xylenol, 2, 4, 6-trimethyl phenol, etc. The order of retention times on the stationary phases capable of forming hydrogen bonding with the phenols would normally be in the order: class (1) > class (2) > class (3) mentioned above and the same is evident from Table 3.

Further, this type of selective retention changes with the functional group of stationary phases in the order: $SH > NH_2 > OH$. An increase in the number of functional OH groups in the molecule of the stationary phase results in increased selectivity for phenols. Their observation indicates that sugars with at least three functional—OH groups gave good separation of phenol-isomers based on the nature of steric hindrance. Some of the general conclusions drawn by Janak and coworkers regarding the analysis of coal tar phenols are as follows:

(1) Single stationary phase is unable to separate all the individual constituents of a mixture of C_6 to C_9 monohydric phenols;

(2) A combination of a non-polar stationary phase, like Apiezon-M grease, and a polar stationary phase, like sugars or modified sugars, is desirable for complete separation;

(3) For the separation of dihydric phenols, like catechol and its homologues; simple sugars, like inositol, mannitol and dulcitol are found good; and

(4) For routine plant analysis of C_6 to C_9 monohydric phenols, dimethyl polysiloxane as stationary phase is suitable.

WORK AT REGIONAL RESEARCH LABORATORY, HYDERABAD

In this Laboratory, work is on hand on the analysis of tar acid mixtures from low temperature tars using gas chromatography. From a study of published literature on single stationary phases capable of separating the simple C_6 to C_9 phenols, the phosphoric esters of phenols seemed to be quite promising. In the present paper the use of tricresyl phosphate with or without the addition of orthophosphoric acid as stationary phase has been reported for the analysis of phenols (b.p. up to 220°C.).

TABLE 3—COMPARATIVE RETENTION VOLUME DATA OF SOME MONOHYDRIC PHENOLS ON DIFFERENT STATIONARY PHASES (Janak and coworkers)

B.P., °C.*	Functional groups	DIMETHYL POLY-SILOXANE $-CH_3$	PHENYL MERCAPTO THIOBIAZOLE† $-SH$ $-C_6H_5$	AMINO GUANIDINE SALICYLATE† $-NH_2$ $-OH$ $-COOR$	BENZYL ARABINOSIDE $-C_7H_7$ $3X-OH$	GLYCEROL† $3X$ $-OH$	γ-LACTONE OF GALACTONIC ACID $-O-$ $3X-OH$	DULCITOL $6X$ $-OH$
	Column temperature °C.	170	160	170	176	160	150	196
181·8	Phenol	1·00	1·00	1·00	1·00	1·00	1·00	1·00
191	*o*-Cresol	1·93	1·23	0·89	1·03	0·60	0·61	0·50
202·2	*m*-Cresol	2·15	1·56	1·41	1·39	0·97	0·98	0·84
201·9	*p*-Cresol	2·15	1·55	1·41	1·36	0·97	0·97	0·83
207·0	*o*-Ethyl phenol	2·52	. .	. .	1·25	0·50	. .	. .
214·0	*m*-Ethyl phenol	2·75	. .	. .	1·99	0·90	. .	. .
219·0	*p*-Ethyl phenol	2·75	. .	. .	1·97	0·92	. .	. .
218·0	2, 3-Xylenol	3·07	. .	1·48	1·72	0·76	0·75	0·54
210·0	2, 4-Xylenol	2·70	1·85	1·20	1·34	0·62	0·56	0·46
210·0	2, 5-Xylenol	2·72	1·85	1·07	1·37	0·53	0·50	0·38
201·0	2, 6-Xylenol	2·63	. .	0·92	0·78	0·33	0·35	0·30
225·0	3, 4-Xylenol	3·34	. .	2·39	2·32	1·26	1·28	0·89
221·5	3, 5-Xylenol	3·27	. .	1·90	1·92	0·96	0·94	0·81

*As reported in the C.T.R.A. data book.

†Retention ratios are corrected for decrease in weight of the stationary phase due to its volatility at given temperatures.

EXPERIMENTAL

Materials. 1. Tricresyl phosphate (technical B.D.H.), distilled at 5 mm. up to a temperature of 150°C. and the residue is used for the experiments; 2. Orthophosphoric acid (Merck); 3. Celite 545 (+120 mesh).

Apparatus. Griffin and George Mk II apparatus. The columns and the catherometer are heated by an electrically regulated air-oven. A flash heater at the point of injection of the sample is heated with a heating element controlled by a Variac transformer.

Method. A slurry is made using requisite quantities of +120 mesh celite 545 and the stationary phase in ethyl ether. The ether is evaporated under gentle stirring and the impregnated celite is heated up to 110°C. Any material finer than 120 mesh is sieved off and the +120 material is packed in the U-tube glass columns using a vibrational motor according to the method of James and Martin[19].

Tricresyl phosphate (15 per cent w/w on celite), a mixture of 5:3 of tricresyl phosphate and orthophosphoric acid, respectively in the ratio of 5:3, 7:3 and 15:5 (8, 10 and 20 per cent w/w on celite) were used as column packings. Experiments were done using nitrogen or hydrogen as carrier gas at column temperatures of 124° and 150°C. and a flow rate of 1·4 to 3·2 litres/hr.

RESULTS AND DISCUSSION

At 124°C., very broad peaks with tailing, were obtained and sharp and well-defined peaks were obtained at 150°C. Typical retention times for 16 phenols (b.p. up to 220°C./760 mm.) on a tricresyl phosphate+orthophosphoric acid in the ratio of 15:5, (20 per cent w/w on celite) stationary phase are given in Table 4. Similar results were observed using 15 per cent w/w tricresyl phosphate alone as stationary phase. It can be seen from Table 4 that the retention times are not in the order of increasing boiling points of the compounds. The *ortho*-alkyl-substituted phenols having boiling points close to *meta*- and *para*-alkyl-substituted phenols emerge much earlier than the latter. The alkyl-substitution in both the 2- and 6-positions further reduced the retention time, e.g. 2, 6-xylenol emerges earlier than *o*-cresol and 2, 4, 6-trimethyl phenol emerges earlier than *ortho*-*n*-propyl phenol. Similar results reported by Eckhardt and Heinze[20], in the G.L.P.C. of pyridine and its homologues were attributed to steric hindrance, where the *ortho*-substitution in the bases prevented hydrogen bond formation with the polar stationary phase (tricresyl phosphate). Brooks[21], on the other hand, using trixylenyl phosphate as stationary phase, had earlier reported that the retention times of the bases were in the order of their boiling points without the stationary phase showing any selectivity.

TABLE 4—RELATIVE RETENTION TIME OF PHENOLS

(B.P. up to 220°C./760 mm.)

[Stationary phase: A mixture of tricresyl phosphate (technical) and orthophosphoric acid in the ratio 15 : 5 (20% w/w on celite); Carrier gas: N_2 (Flow rate 3·2 litres/hr); Column length: 6 ft (¼ in. diam.); Wt of packing: 15·15 g.; Column Temp. 150°C.; Detector: Thermal conductivity type; Inlet pressure: 635 mm.; Outlet pressure: 101 mm. Bridge current: 100 milli amps. Recorder speed: 6 in./hr]

Name	B. P.* C.°/760 mm.	Relative retention time (Phenol = 1)
Phenol	181·8	1
o-Cresol	191·0	1·25
m-Cresol	202·2	1·65
p-Cresol	201·9	1·68
2, 6-Xylenol	201·0	1·14
Guaiacol	205·0	0·82
o-Ethyl phenol	207·0	1·79
2, 4-Xylenol	210·0	1·92
2, 5-Xylenol	210·0	2·00
o-Isopropyl phenol	211·0	2·36
2, 3-Xylenol	218·0	2·54
m-Ethyl phenol	214·0	2·82
p-Ethyl phenol	219·0	2·81
3, 5-Xylenol	221·5	2·82
o-n-Propyl phenol	220·5	2·43
2, 4, 6-Trimethyl phenol	220·0	1·71

*As reported in C.T.R.A. data book.

Another interesting observation is that the monomethyl ether of catechol (guaiacol) emerges earlier than phenol even though the boiling point is about 24°C. higher than the latter. This, perhaps, may be due to low solubility of guaiacol on the stationary phase. Carruthers (loc. cit.) also reported that dimethoxy-benzenes emerged along with xylenyl ethers on the Apiezon M grease as stationary phase even though the former had higher boiling point. According to him this was, probably, due to the increased solubility of the xylenyl ethers on the Apiezon M grease. As the stationary phase shows selectivity towards *m*- and/or *p*-substituted phenols, good separation of close boiling mixtures, e.g. of 2, 6-xylenol from its mixture with *m/p*-cresols and of 2, 4, 6-trimethyl phenol from its mixture with 3, 5-xylenol is obtained. However, in a mixture of all the phenols (b.p. up to 220°C.), separation was only partial which was due to the overlapping caused by the earlier emergence of *ortho*-substituted compounds irrespective of their boiling points.

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Ultraviolet Spectrophotometric Studies of Isomeric Cresols : Part I—Ferric Cresolate Complexes

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Ultraviolet absorption spectra of isomeric cresols and ferric cresolate complexes have been studied. Characteristic absorption maxima of the complex species are obtained. A straight line relationship is shown between concentration and optical density although in most of the cases these lines do not pass through the origin.

Carney and Sanford[1] developed a spectrophotometric method for the estimation of isomeric cresol mixtures in iso-octane, while Pearson[2] separated the cresols by partition chromatography and estimated them by ultraviolet spectrophotometry.

Ferric ion is known to form colour complexes with phenols and cresols. Brode and Wesp[3], and Banerjee and Haldar[4] worked on the constitution of the complex species, but, because their colour fades instantaneously, no successful spectrophotometric method in the visible region could be evolved. A study of these complex species by ultraviolet spectrophotometric method has now been made with a view to develop a suitable method for the estimation of isomeric cresols.

ULTRAVIOLET ABSORPTION SPECTRA OF CRESOLS AND FERRIC CRESOLATE COMPLEXES

The spectroscopic purity of the isomeric cresols used in this study was determined from their u.v. spectra in spectro grade cyclohexane and iso-octane. U.V. spectra of isomeric cresols using different solvents are shown in Table 1.

TABLE 1—ULTRAVIOLET ABSORPTION SPECTRA OF ISOMERIC CRESOLS IN DIFFERENT SOLVENTS

Cresol	Solvent	Max. in mμ
m-Cresol	Water	273, 279
	Cyclohexane	273, 278
	Iso-octane	273, 279
o-Cresol	Water	272, 278
	Cyclohexane	272, 279
	Iso-octane	273, 279
p-Cresol	Water	278, 286
	Cyclohexane	275, 278, 286
	Iso-octane	278, 285

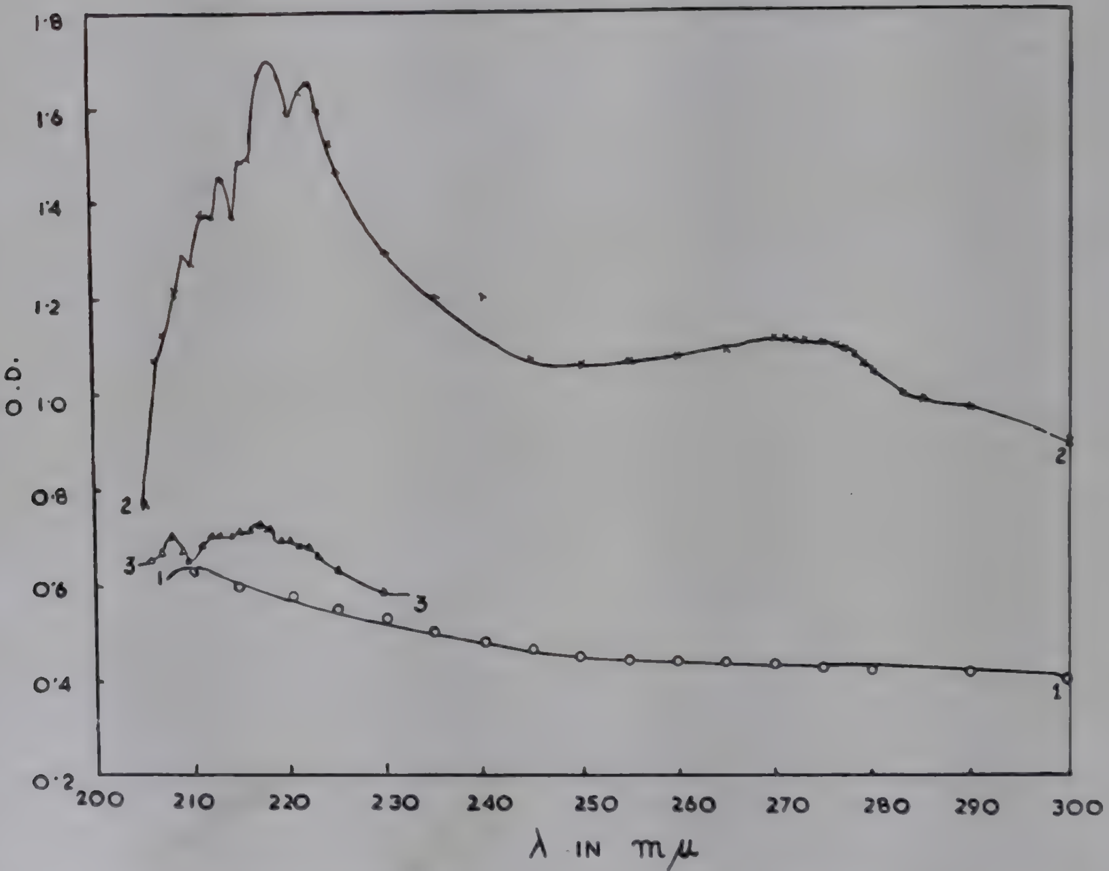

FIG. 1—ULTRAVIOLET ABSORPTION SPECTRA OF FERRIC ION AND ITS MIXTURE WITH CRESOLS: (1) Ferric ion; (2) Ferric ion, *m*-, *o*- and *p*-cresols in water in 3:1:1:1 molar proportion: (3) Mixture No. 2 diluted 5 times

U.V. spectra of ferric ion (from ferric ammonium sulphate A.R.) and of mixture of ferric salt, *m*-cresol, *o*-cresol, and *p*-cresol in water in 3:1:1:1 molar proportion in two different concentrations were taken. A low intensity absorption maximum was observed below 210 mμ for ferric ion. Four intense absorption maxima at 218, 213, 209 and 223 mμ and three low intensity absorption maxima at 271, 277 and 284 mμ were observed for the above mixture. When the mixture is diluted five times with the solvent, the position of the absorption maxima is not changed appreciably. These spectra are shown in Fig. 1. Appropriate wavelengths were chosen in the vicinity of the absorption maxima and the Beer's law was verified. A straight line relationship is obtained but in most of the cases, the lines do not pass through the origin. A method based on these results is being worked out for the identification and estimation of isomeric cresol mixtures.

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The Nitrogenous Bases in Low Temperature Tar

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The character and composition of the heterocyclic bases occurring in low temperature tar have been studied and compared with those present in high temperature tar. Twenty-nine compounds constituting about 90 per cent of the total bases have been identified and a few bases have been quantitatively estimated.

During the carbonization of coal, its nitrogen content seldom exceeding 1·8 per cent of the pure coal substance, gets converted into nitrogenous compounds and distributed in the various fractions of the pyrolysis products. In high temperature carbonization (h.t.c.), the major part of the nitrogen in coal appears in the form of ammonia, hydrocyanic acid and free nitrogen, while a small fraction appears in the form of heterocyclic bases, commonly referred to as 'coal tar bases'. These bases, generally of complex composition, occur as mixtures of pyridines, picolines (α, β and γ), lutidines, aniline, quinolines, quinoline derivatives and higher bases. The quantity of bases produced is generally very small and, further, on account of their widely varying boiling points and solubility in water and oils, the pyridine bases get distributed in tar, gas stream ammoniacal liquor, benzole, etc. The distribution and composition of these bases occurring in the byproducts of h.t.c. has been studied in this laboratory in the context of current interest in the development of drug industry in India which has called for an assessment of the indigenous potential for production of γ-picoline and other pyridine bases, all of which are valuable as intermediates in the manufacture of a wide variety of drugs and fine chemicals.

The temperature of carbonization has a profound effect on the yield and composition of the gaseous and liquid by-products. While it is well known that yield of liquid by-product is almost doubled when coal is carbonized at lower temperatures, comparatively little is known about the composition of these by-products and, in particular, about the nitrogenous heterocycles contained in them. The yield of tar bases as a function of carbonizing temperature was studied for British coals by Sinhatt and coworkers[1], who observe that the maximum yield of tar bases is obtained at temperatures of 600-650°C., while, according to other workers h.t.c. processes operating above 850°C. give maximum conversion of nitrogen to useful compounds. A number of primary and tertiary amines have been isolated[2–3] from low temperature tar, but publications on the subject are few and a proper correlation of the nitrogen heterocycles with conditions of carbonization has never been attempted.

The primary object of operating low temperature carbonization (l.t.c.) processes is normally to produce a free-burning non-friable and smokeless semicoke suitable for use in all types of domestic grates and appliances. Coincident with the production of semicoke is the enhanced yield of liquid products differing in quantity and composition from the liquid products obtained at high and medium temperatures. While the production of liquid products is not the primary purpose of l.t.c., the economics of the process hinges on the successful exploitation of the valuable contents of l.t. tar. A complete investigation of the composition of l.t. tar has, therefore, been undertaken. The results of studies on the nitrogenous bases are reported here.

EXPERIMENTAL

A sample of tar obtained by l.t.c. of coal (600°C.) from Koithee seam, Jamuria colliery and Hatnal seam, Seetalpur colliery was selected for the investigation. The techniques and procedures employed for isolating the tar bases and their identification and estimation were similar to those described earlier[4].

The tar was distilled in a 4-gal. still and the light oil (up to 210°C.), middle oil (210-270°C.), and anthracene oil (270-360°C.) were collected separately. It was found necessary to precede the extraction of tar bases in the oils with alkali treatment to remove tar acids and to break up the rather stable phenol-pyridine type complexes. After removing tar acids with 15-20 per cent caustic soda solution, the tar bases were extracted with 15-20 per cent sulphuric acid. Slow neutralization of the base sulphates with 15 per cent caustic soda solution precipitated out the tar bases. Subsequent extraction with benzene, followed by distillation of the benzene in a fractionating column, yielded crude bases. The tar oils boiling up to 270°C. and the oils boiling between 270° and 360°C. were worked up separately for the bases. The crude bases were fractionated in a packed column of 1 in. diam. and 24 in. long packed with glass beads and provided with a still head. Each fraction was characterized by its refractive index, density, UV and IR spectra. Densities were determined pyknometrically and refractive indices with an Abbe refractometer. UV spectra were taken with a Unicam instrument in aqueous solution using 1 cm. cells and IR spectra with a Leitz double beam spectrophotometer provided with a rock-salt prism. Samples were run as pure liquids and as solutions in carbon disulphide and carbon tetrachloride, quantitative analysis being accomplished by the base line procedure.

Besides aiding in the characterization of each fraction, the infra-red spectra also made it possible to follow the course of distillation by assessing the sequence and relative enrichment of the various components in different fractions. The frequencies of the diagnostic bands were determined from the spectra of either authentic samples or from published spectra.

Besides spectroscopic analysis, a few compounds were characterized chemically as well. The pyridine content of the crude bases was directly estimated by a colorimetric procedure[6], in which the intensity of the colour developed by pyridine on heating with potassium hydroxide and chloroform was measured. The picolines, collidines and lutidines do not interfere in the determination. The presence of piperidine was confirmed by the preparation of the *para*-toluenesulphonyl derivative. γ-Picoline was also quantitatively estimated[7] by colorimetric analysis of the purple complex that it forms with 2, 4-dinitrochloro-benzene, acetamide and 2, 6-lutidine in alcoholic solution using a Spekker absorptiometer. Confirmation of the N-H group in the sample was obtained by deuteration of the aniline fraction followed by spectroscopic examination. Refluxing the sample with heavy water under base-catalyzed conditions resulted in a considerable decrease of the 3300-3500 $cm.^{-1}$ (N-H stretching) band and production of two new bands at 2450 and 2600 $cm.^{-1}$, where the N-D stretching vibration occurs.

The intense colour of the acid extract excluded the possibility of using any indicator and, unlike in the case of h.t. tar oils, the base content could not be determined by titration but had to be estimated by isolation. Processing an adequate amount of tar yielded a few hundred millilitres of the mixture of bases in each case, which were then subjected to detailed analysis as stated above. Despite the complexity of the tar base mixtures, careful fractionation followed by spectroscopic analysis enabled a large number of the individual tar bases to be identified and estimated.

RESULTS AND DISCUSSION

The distillation characteristics of the tar sample and the base content of the tar oil cuts (expressed as wt per cent of the oil and wt per cent of the dry tar) are given in Table 1. Figs. 1, 1A and 2, 2A illustrate distillation characteristics of bases isolated from tar oils boiling up to 270°C. and 270-360°C. respectively. The two figures constitute a 'base distribution spectrum',

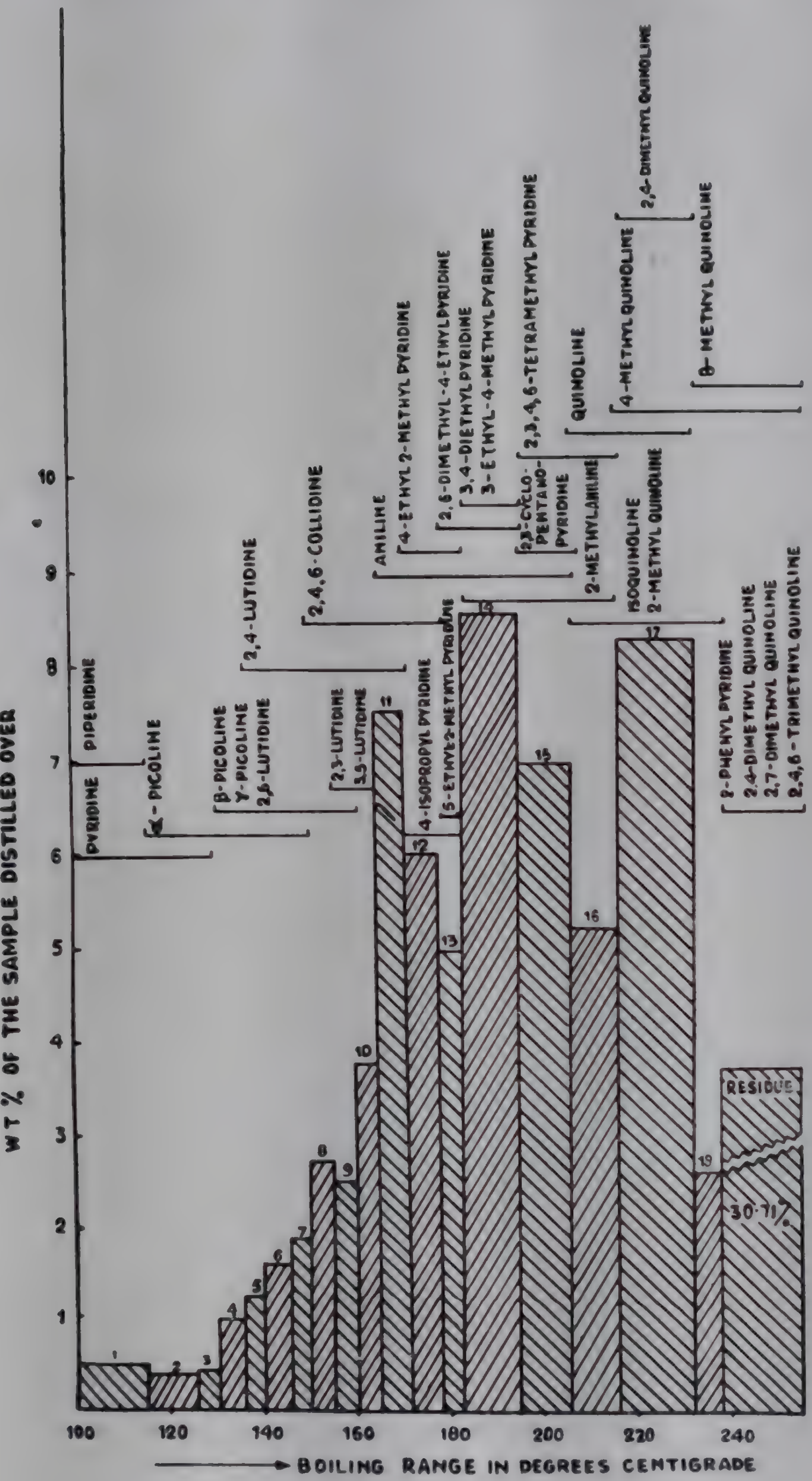

FIG. 1—DISTILLATION CHARACTERISTICS OF THE BASES OBTAINED FROM LOW TEMPERATURE CARBONIZATION TAR OIL : I.B.P.—270°C.; Column size—24 in. × 1 in.; Packing—Glass beads; Reflux ratio—20:1

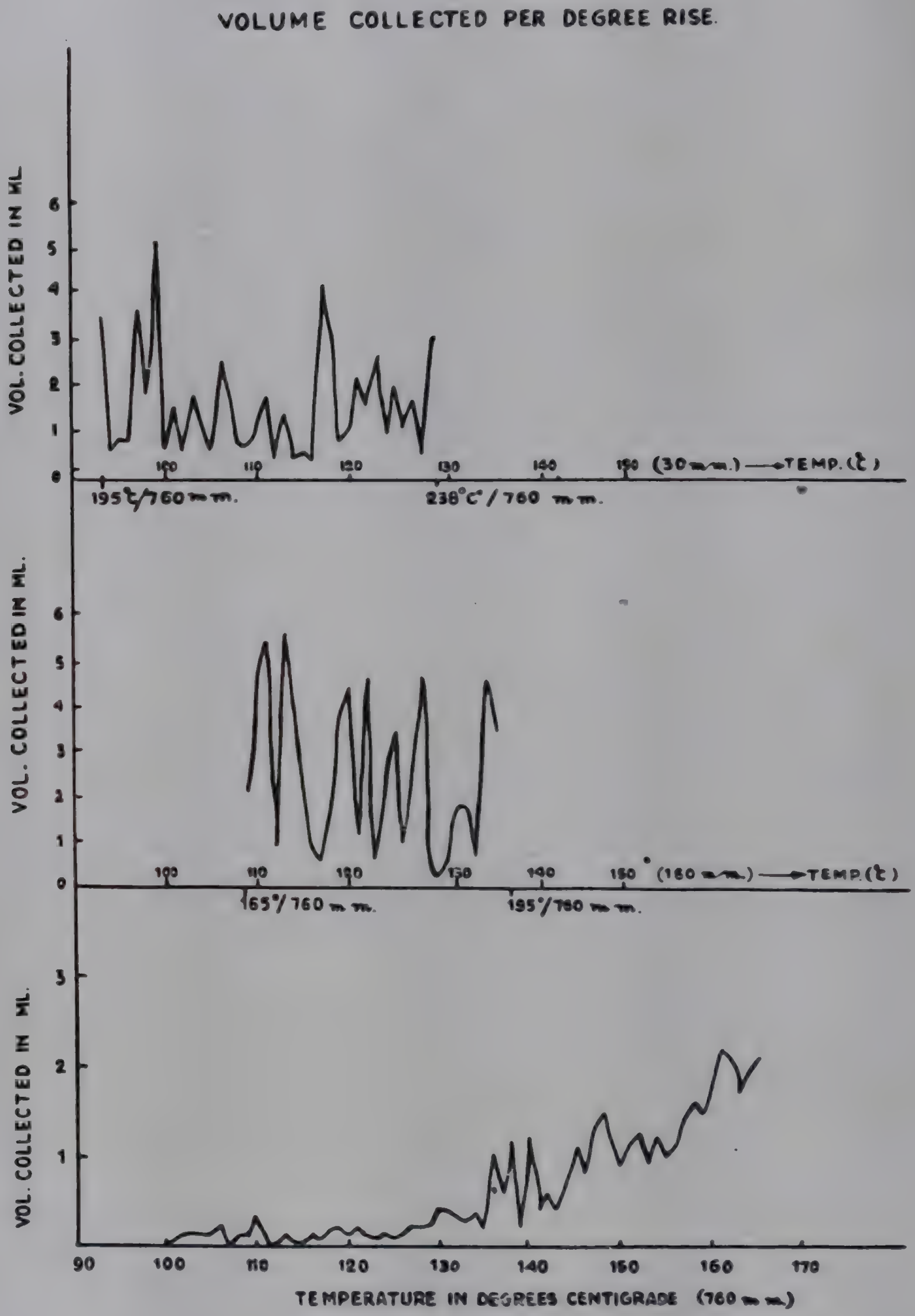

FIG. 1A—DISTILLATION CHARACTERISTICS OF THE BASES OBTAINED FROM LOW TEMPERATURE CARBONIZATION TAR OIL : I.B.P.—270°C.; Column size—24 in. × 1 in.; Packing—Glass beads; Reflux ratio—20: 1

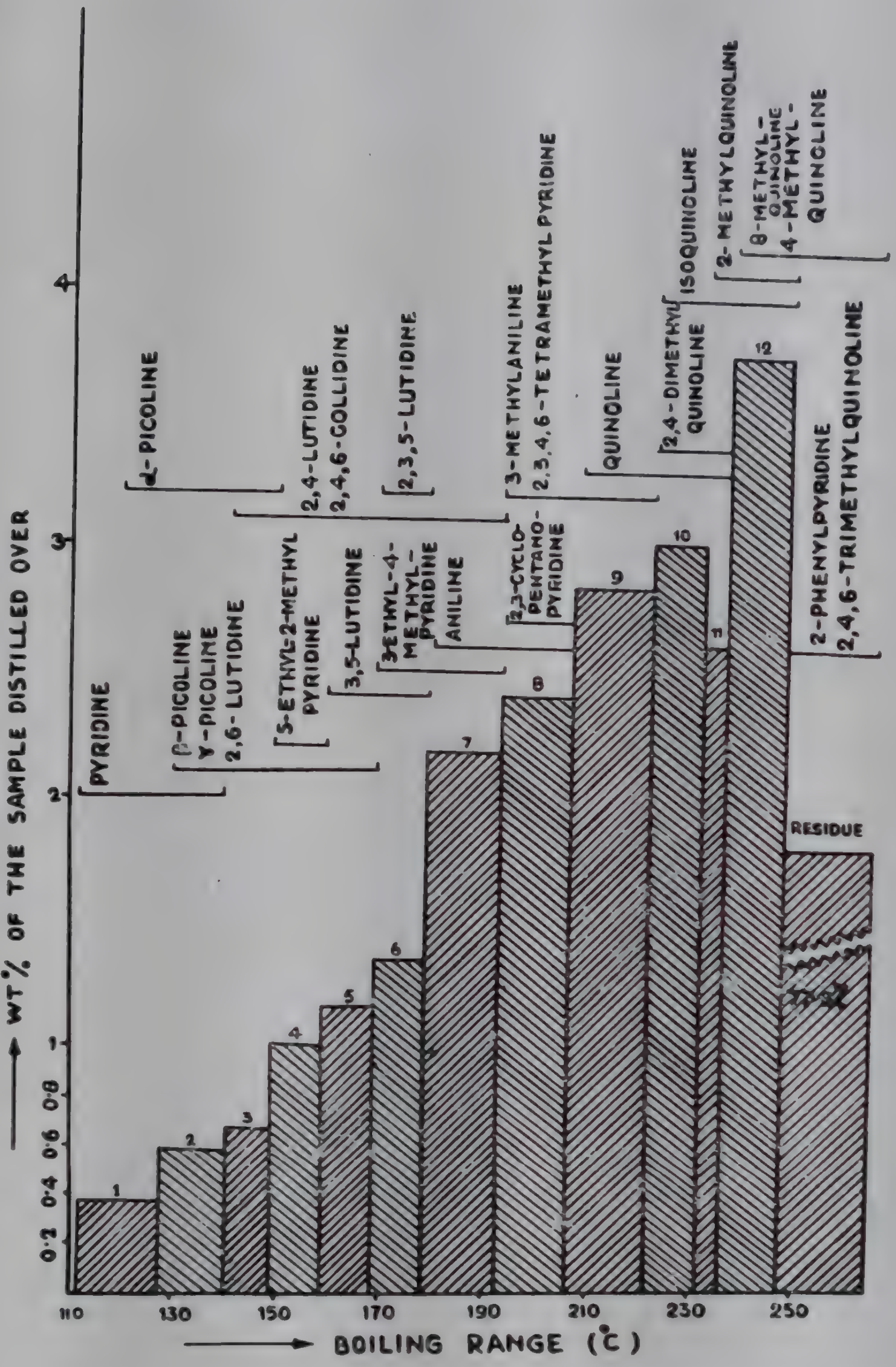

Fig. 2—Distillation characteristics of the bases obtained from low temperature carbonization tar oil : B.P.—270°—360° C.; Column size—24 in. × 1 in.; Packing—Glass beads; Reflux ratio—20:1

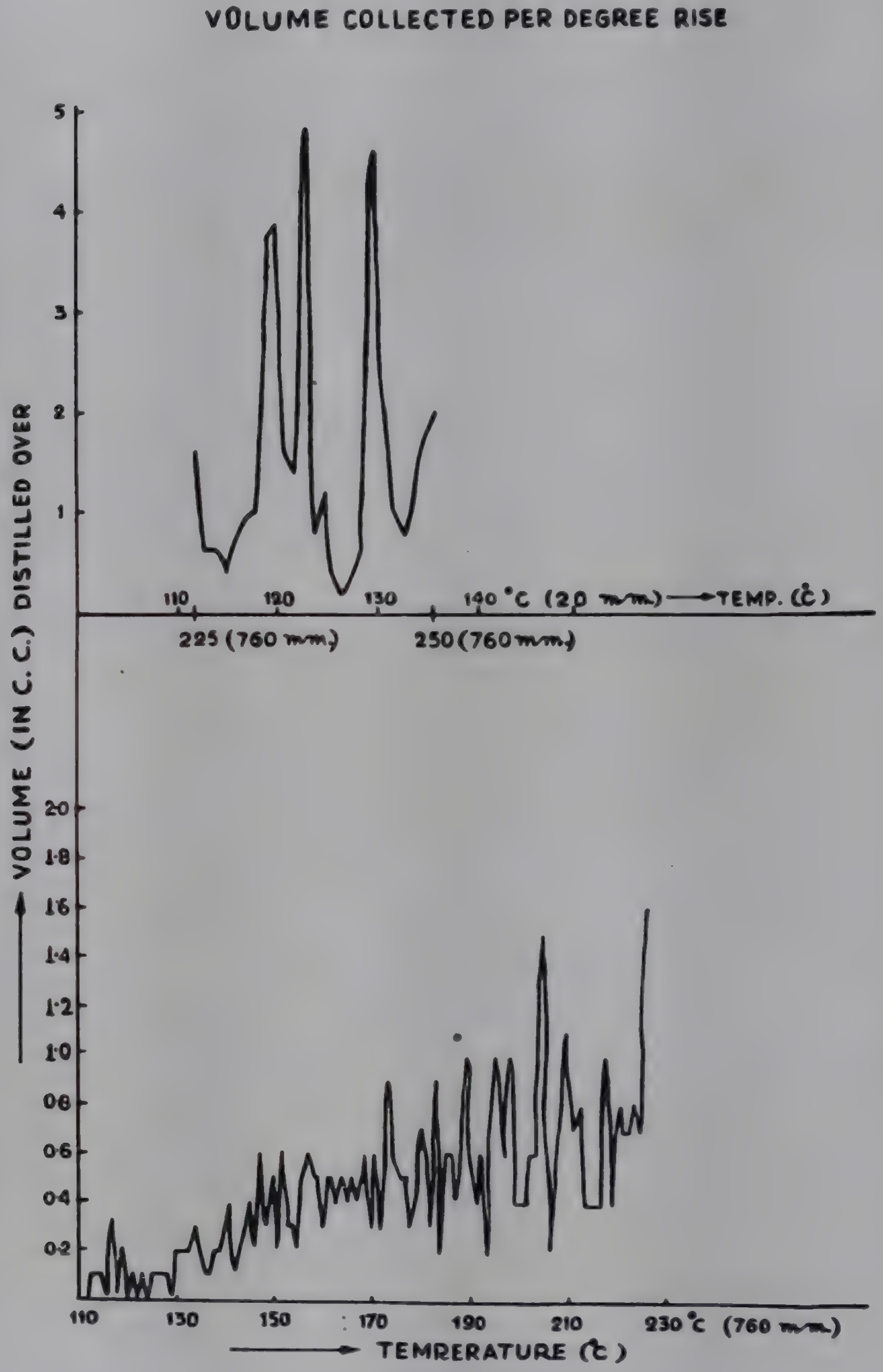

Fig. 2A—Distillation characteristics of the bases obtained from low temperature carbonization tar oil: B.P.—270°—360°C.; Column size—24 in. × 1 in.; Packing—Glass beads; Reflux ratio—20: 1

TABLE 1—DISTILLATION CHARACTERISTICS AND DISTRIBUTION OF BASES IN L.T. TAR

Boiling range	Distillate, %	Base Expressed as wt % of the oil	Content Expressed as wt % of the dry tar
Up to 210°C.	8·15	3·39	1·20
210-230°C.	12·85		
230-270°C.	14·52		
270-300°C.	12·60	3·48	1·33
300-360°C.	25·53		
Pitch	25·08	..	..
Loss	1·27	..	..
Total	..	..	2·53

illustrating the range over which specific components distilled over, the volume collected per degree rise, and giving a plot of the wt per cent of each fraction against boiling range. Attention is drawn to the occurrence of low-boiling bases like piperidine, α-, β-, and γ-picolines, lutidines and collidines in tar oils boiling above 270°C., contrary to what would be expected from boiling point considerations. A similar observation was earlier reported[4] in the case of the anthracene oil obtained from h.t. tar. The phenomenon is explained by assuming that the bases are present in tar as stable complexes with a variety of phenols which are present in l.t. tar in abundance, and, therefore, what appears to determine the range in which a base distils over is not the boiling point of the nitrogenous base itself, but that of the particular pyridine-phenol complex.

Table 2 lists the individual compounds identified. Of the 29 compounds identified to be present, one is a saturated base, piperidine, 18 are pyridine and its alkyl derivatives, 2 are anilines and 8 belong to the quinoline and isoquinoline group. It is believed that these compounds account for more than 90 per cent of the bases present in the tar distillates. Quantitative analyses are reported for pyridine; α-, β-, and γ-picoline; 2,6-lutidine; 2, 4, 6-collidine; aniline and quinoline. The other components were not quantitatively estimated.

The total base content of the tar was found to be 2·53 per cent. Even though 19 of the 29 compounds identified are one-ring systems, primarily pyridine and its alkyl derivatives, these probably account for less than one-fourth of the total tar bases, quinoline and its derivatives constituting the major part. Piperidine has been detected only in traces and it is not unlikely that even if this saturated compound is produced as a primary product of coal pyrolysis, it undergoes transformation into the much more

TABLE 2—INDIVIDUAL BASES IN LOW TEMPERATURE TAR

No.	Compound	Quantity (expressed as wt % of total tar bases, i.e. bases obtained from all oils, b.p. I.B.P. 360°C.) present in the			P. P. M. in tar	Diagnostic wave-lengths, microns
		Oils, b.p. up to 270°C.	Oils, b.p. 270–360°C.	Total oils		
1.	Piperidine	Traces	..	Traces	..	..
2.	Pyridine	0·24	0·10	0·34	79·2	14·30
3.	α-Picoline	0·70	0·21	0·91	212·0	13·35
4.	β-Picoline	0·22	0·16	0·38	88·5	12·80
5.	γ-Picoline	0·50	0·14	0·64	149·1	12·60
6.	2, 6-Lutidine	1·94	0·49	2·43	566·2	13·00
7.	2, 4-Lutidine	Major	Major*	Major	..	12·30
8.	3, 5-Lutidine	Traces	Traces	Traces	..	14·15
9.	2, 3-Lutidine	Traces ?	Traces ?	Traces ?	..	12·80
10.	2, 4, 6-Collidine	3·23	0·80	4·03	939	11·93
11.	4-Isopropylpyridine	Traces	..	Traces	..	11·25
12.	4-Ethyl-2-methylpyridine	Minor	Traces	Traces	..	11·90
13.	2, 6-Dimethyl-4-ethylpyridine	do	do	do	..	11·70
14.	5-Ethyl-2-methylpyridine	do	do	do	..	12·15
15.	3, 4-Diethylpyridine and/or	do	do	do	..	12·18
16.	3-Ethyl-4-methylpyridine					
17.	Aniline	0·65	0·20	0·85	198·1	13·40; 14·55
18.	3-Methylaniline	Minor	Minor*	Minor	..	13·00; 14·55
19.	2, 3, 4, 6-Tetramethylpyridine	Traces	Traces	Traces	..	11·67
20.	2, 3-Cyclopentanopyridine	Traces	Traces	Traces	..	12·80
21.	Quinoline	0·69	1·27	1·96	456·7	12·47
22.	Isoquinoline	Major	Major	Major	..	12·15
23.	2-Methylquinoline	Major	Major	Major	..	12·25
24.	4-Methylquinoline	Major	Major	Major	..	13·25; 12·00
25.	5-Methylquinoline	Minor	Major	Major	..	12·70
26.	2, 4-Dimethylquinoline	Major	Major	Major	..	11·65; 13·20
27.	2-Phenylpyridine	Major	Major	Major	..	13·4
28.	2, 4, 6-Trimethylquinoline	Major	Major	Major	..	12·13
29.	2, 7-Dimethylquinoline	Minor	Minor	Minor	..	11·97

Total base content of the tar (i.e. bases recoverable from the tar oils I.B.P. to 360°C. =2·53%) expressed as wt % of dry tar.

*Where the concentration is likely to be more than 5%, the compound has been classified as a major constituent, and where the concentration is believed to be less than 5%, the compound has been rated as a minor component.

stable pyridine ring system by thermal dehydrogenation. This hypothesis is in agreement with the finding that piperidine has not been detected even in traces in the products of h.t.c. as can be seen from Table 3, where the individual nitrogen heterocycles present in a typical h.t. tar (West Bengal Coke-ovens, Durgapur) and their concentrations are reported. The concentration of pyridine itself in the total tar oils from l.t. tar is less than that of any of the three picolines (Table 4). Among the picolines, α-picoline appears to be the predominant isomer and β-picoline the least abundant. Of the six different dimethyl pyridines, four were identified, 2 : 6 and 2 : 4-lutidine

TABLE 3—INDIVIDUAL BASES IN DURGAPUR TAR

No.	COMPOUND	% IN THE TOTAL TAR BASES	P. P. M. IN TAR	DIAGNOSTIC WAVE LENGTHS, microns
1.	Pyridine	0·77	153·2	14·30
2.	α-Picoline	0·33	65·6	13·35
3.	β-Picoline	0·59	117·4	12·80
4.	γ-Picoline	0·93	185·0	12·60
5.	2, 6-Lutidine	0·24	47·7	13·00
6.	s-Collidine	0·53	105·4	11·93
7.	2, 4-Lutidine	Minor component*	..	12·30
8.	Aniline	0·74	14·72	13·40
9.	3-Methylaniline	Minor component	..	13·00 14·55
10.	Quinoline	17·33	3448·6	12·47
11.	Isoquinoline	Major component	..	12·15
12.	2-Methylquinoline	Minor component	..	12·25
13.	2, 4-Dimethylquinoline	do	..	11·65 13·20
14.	4-Methylquinoline	do	..	13·25 12·00
15.	Phenanthridine	Major component	..	13·42
16.	Acridine	do	..	13·60
17.	7, 8-Benzoquinoline	do	..	12·05
18.	2, 7-Dimethylquinoline	Minor component	..	11·97
19.	5, 6-Benzoquinoline	Major component	..	13·35

*Major and minor denote the same classification as indicated in Table 2.

TABLE 4—COMPARISON OF INDIVIDUAL COMPOUNDS IDENTIFIED IN H.T. AND L.T. TARS

No. Compounds common to both H.T. and L.T. tars	No. Compounds present in H.T. tar but absent in L.T. tar	No. Compounds present in L.T. tar but absent in H.T. tar
1. Pyridine	1. Phenanthridine	1. Piperidine
2. α-Picoline	2. Acridine	2. 3, 5-Lutidine
3. β-Picoline	3. 7, 8-Benzoquinoline	3. 2, 3-Lutidine
4. γ-Picoline	4. 5, 6-Benzoquinoline	4. 4-Isopropylpyridine
5. 2, 6-Lutidine		5. 4-Ethyl-2-methylpyridine
6. 2, 4-Lutidine		6. 2, 6-Dimethyl-4-ethylpyridine
7. 2, 4, 6-Collidine		7. 5-Ethyl-2-methylpyridine
8. Aniline		8. 3, 4-Diethylpyridine
9. 3-Methylaniline		9. 3-Ethyl-4-methylpyridine
10. Quinoline		10. 2, 3, 4, 6-Tetramethylpyridine
11. Isoquinoline		11. 2, 3-Cyclopentanopyridine
12. 2-Methylquinoline		12. 8-Methylquinoline
13. 4-Methylquinoline		13. 2-Phenylpyridine
14. 2, 4-Dimethylquinoline		14. 2, 4, 6-Trimethylquinoline
15. 2, 7-Dimethylquinoline		

being present in appreciable quantities and 3, 5-, and 2, 3-lutidine only in traces. The occurrence of these isomers is not what would be expected on the basis of a random distribution and the reasons favouring the preferential formation of particular isomers are not understood. In so far as the symmetrical trimethyl pyridine (2 : 4 : 6-) constitutes as much as 4% of the total bases in the tar oils, the complete absence of the other four isomeric trimethyl pyridines is surprising, and it is doubtful whether the greater stability of symmetrical collidine can be considered to be an adequate explanation. A few of the ethyl methyl pyridines were observed to occur in traces, but no pyridine derivatives with alkyl chain lengths greater than two carbon atoms were observed with the exception of 4-isopropyl pyridine (traces). It has been suggested that under the conditions of formation of the tar (>500°C.) alkyl chains of three of four carbons could conceivably cyclize to form fused saturated rings, as exemplified by cyclopentanopyridines and tetrahydroquinolines which in turn might undergo thermal dehydrogenation to yield the completely aromatic derivatives. Aniline and 3-methyl aniline are the only amino derivatives that could be detected. Quinoline constituted only about 2 per cent of the total bases, though its alkyl derivatives were found to be present in greater abundance, 2, 4- and 8-methyl quinoline and 2, 4, 6-trimethyl quinoline being classified as major constituents. No derivative of isoquinoline could be isolated or identified, but isoquinoline itself is believed to be present in appreciable quantities. No evidence could be obtained for naphthylamine and benzylaniline systems.

While the total base content (2·53 per cent) of l.t. tar is of the same order of magnitude as that observed for h.t. industrial tars (1·99 to 2·98 per cent), it is observed from a comparison of Tables 2 and 3 that the composition of the l.t. tar bases is significantly different from that of the h.t. tar bases. A greater variety of heterocyclic bases are seen to be present in l.t. tar, for as against the 19 compounds identified in Durgapur tar 29 compounds are reported in Table 2 for l.t. tar. The nitrogenous bases identified in both high and low temperature tars are divided in Table 4 into 3 categories, first those that are common to both the tars, and second and third, those that are exclusive to each tar. While all the alkyl pyridine derivatives present in h.t. tar also occur in l.t. tar, the latter in addition contains 12 more alkyl pyridines not found in the former. The greater abundance and variety of the simpler alkyl pyridines and the marked absence of phenanthridine, acridine, 7 : 8-, and 5 : 6-benzoquinolines in l.t. tar appears to indicate that the higher bases found as major components in h.t. tar are probably formed by the cracking and polymerization of the simpler alkyl pyridine derivatives initially formed during carbonization. It is likely that because of the greater degree of substitution and branching, isopropyl pyridine and ethyl methyl pyridines found exclusively in l.t. tar are more liable to undergo thermal fragmentation and ring fusion at higher temperatures in contrast to the simple picolines and anilines which are common to both the tars.

The concentrations of pyridines and the three picolines in both high and low temperature tars are of the same order of magnitude (80 to 200 p.p.m. based on the tar), but a relevant point to be considered in assessing the recovery potential of the bases is that l.t.c. yields per ton of coal nearly three times the tar obtained in h.t.c. The lutidine content of l.t. tar on the other hand, is much higher than that of h.t. tar, the value for 2, 6-lutidine in the two tars being 566 and 48 p.p.m. respectively. 2, 4-Lutidine has been classified as a major component (>5 per cent) of the l.t. tar bases, while it is reported as a minor component of the h.t. tar bases. Collidine too occurs in much greater abundance in l.t. tar (939 p.p.m.), while for h.t. tar it is only 105 p.p.m. In addition to the theoretical interest attached to the greater abundance of the methyl pyridines in the products of l.t.c., these findings are important in that they illustrate the superiority and suitability of l.t. tar as an attractive source for lutidines and collidines, commercially in demand as solvents, reagents and intermediates. While the concentration of quinoline in l.t. tar is only one-eighth of its concentration in h.t. tar, alkylated quinolines are present in greater abundance in l.t. tar. Quinoline constitutes only about 2 per cent of the total tar bases in l.t. tar while methylated quinolines account for more than 30 per cent. In h.t. tar the corresponding figures are 17 per cent for quinoline but less than this value for its methyl derivatives.

From these considerations it would appear that alkylated quinolines are amongst the products of primary pyrolysis from which quinoline may be formed by thermal degradation. It was earlier suggested that phenanthridine, acridine, 7 : 8-, and 5 : 6-benzoquinolines which are exclusive to h.t. tar are probably formed at least in part by the degradation and polymerization of those alkyl pyridines that are exclusive to l.t. tar. Pyridine itself can be pictured as being formed by the condensation of two molecules of acetylene and one molecule of hydrogen cyanide, both of which are known to be present in the products of coal pyrolysis. α-Picoline can be conceived as being produced from two molecules of acetylene and one molecule of methyl cyanide, while β- and γ-picolines could be built up by the union of a molecule of acetylene with one molecule each of methyl acetylene and hydrogen cyanide. Similarly, the lutidines and collidines and ethyl pyridines could be pictured as being synthesized from the appropriate derivatives of hydrocyanic acid and acetylene. The foregoing mechanism is, however, purely speculative, and it could very well be that rather than being synthesized from the acetylenes and hydrocyanic acid, pyridine and its alkyl derivatives are primary products of coal pyrolysis and partially reflect the mode of combination of nitrogen in coal.

It is obvious from a comparison of Tables 2 and 3 that the recovery of bases from l.t. tar is likely to be more profitable than that from high temperature tar, because of the more favourable distribution of the different bases in relation to demand and projected utilization. The pattern of use of these tar bases has been changing rapidly during the last few years. The current U.S. production of pyridine is about 3 million lb. and of the three isomeric picolines put together more than one million lb. About 25 per cent of the refined pyridine is being used for the preparation of water repellent agents (Zelan or Velan); about 40 per cent for various medicinal products such as antiseptics (cetyl and lauryl pyridinium chlorides), sulfa-pyridine (noted for its bacteriostatic activity), antihistamine drugs such as pyribenzamine and for the preparation of 2, 6-diamino-3-phenylazo pyridine hydrochloride, a pyridine dye used as a urinary analgesic and antiseptic, and the remainder used in miscellaneous ways for reduction to piperidine, for denaturing alcohol, for conversion to special chemicals for rubber industry, for synthesis of various detergents, as a corrosion inhibitor and as a reagent and solvent in organic chemistry and for the preparation of pyridine arsenals used in respiratory infections. The demand for α-picoline, an intermediate in the manufacture of 2-vinyl pyridine, has outstripped the supply since the recent finding that 2-vinyl pyridine produces a superior rubber when substituted for styrene in copolymerization with acrylonitrile. The production of nicotinic acid (an ingredient of vitamin B complex) obtained by the oxidation of β-picoline amounted to a million lb. in 1958. The U.S. consumption of coramine (nicotinic acid, N-N-diethylamide) was 30,000 lb. in 1957. Commercially, nicotinic acid is also produced by the oxidation of quinoline and decarboxylation of the resulting quinolinic acid. Isonicotinic acid obtained by the oxidation of γ-picoline has recently assumed importance because of the antitubercular action of its hydrazide. The requirement of this drug in India has been estimated at 100,000 lb. per year. The chief importance of aniline lies in its value as an intermediate in the manufacture of dyes, pharmaceuticals and rubber chemicals. The lutidines and collidines find application as reagents, organic solvents and reaction intermediates. Quinoline and its derivatives serve as intermediates in the manufacture of fabric dyes, cyanine dyes for sensitive photographic plates, synthetic medicinals, such as local anaesthetics and antimalarials, fungicides and mildew-proofing agents (e.g. copper chelate of 8-quinolinol). Both quinoline and isoquinoline are strong collectors of talc and are used as flotation agents. They also find application in the dephenolization of waste liquors from the carbonization of coal by the Holley-Mott and Lownstein processes.

The recovery of bases from tar on an industrial scale is likely to be economic only if planned on an integrated basis. There is an immediate demand in the indigenous pharmaceutical industry for γ-picoline, but while recovering it, other tar bases will be produced in much larger quantities than γ-picoline itself so that production and utilization of the other products must form an integral part of the project. The other bases will be required for the growing chemical industry in India, particularly for drugs, dye-stuffs, rubber, plastics, etc. Though there is as yet no l.t.c. unit in the country working on an industrial scale, it is necessary to think in terms of by-product recovery as the decision to install l.t.c. plants during the next plant period is likely to hinge on the degree of credit that can be given for recoverable by-products.

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Chlorination of Coal Tar Acids : Part I

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The low temperature tar contains about 30 per cent tar acids, consisting mainly of cresols, xylenols and high boiling tar acids of high bactericidal value. The literature on the use of xylenols and high boiling tar acids with and without chlorination is reviewed.

The results of chlorinating a xylenol-cut tar acid fraction obtained from a Lurgi-Spuelgas low temperature carbonization pilot plant working at the Regional Research Laboratory, Hyderabad, are presented.

The low temperature (l.t.) tar produced from the 25 ton/day Lurgi-Spuelgas low temperature carbonization (l.t.c.) pilot plant operating at the laboratory, contains about 30 per cent tar acids, consisting mainly of cresols, xylenols and high boiling tar acids (HBTA) of high bactericidal value[1]. Alkali-soluble tar acids boiling from 230° to 355°C. and above are broadly termed HBTA and form a complex mixture of several tar acids mostly homologues of monohydric phenols. Of these, trimethyl phenol, 3-methyl-5-ethyl phenol, hydroxy hydrindenes, diphenols and naphthols among the monohydric and catechols, resorcinols and hydroquinones among dihydrics have been reported as major constituents in 230-300°C. fraction[2].

The uses of phenols and cresols are well established in industries like plastics, dyes and intermediates, antiseptics, pharmaceuticals, etc. The xylenols and HBTA are used to a limited extent and mostly in the preparation of disinfectants and antiseptics. In recent years modified tar acids, mostly chlorinated products, have assumed greater industrial importance. The use of pentachloro phenol[3] (PCP) for wood preservation, parachloro meta cresol[4] (PCMC), parachloro meta xylenols[5] (PCMX) and dichloro meta xylenols[6-8] (DCMX) as preservatives in cosmetics, soaps, pharmaceuticals and other industries is well known.

The literature on chlorination of tar acids is limited and mostly covered by patents. The present paper gives a review of the literature and describes the results of chlorinating a xylenol-cut of tar acids obtained from l.t. tar.

Chlorination, in general, is an exothermic reaction and the heat of reaction in substitutive chlorination is reported to be in the range of —23000 to —27000 cals. regardless of the nature of the organic molecule[9]. The position of chlorine in the molecule, i.e. in nucleus or in the side chain depends upon several factors like unsaturation in molecules, temperature and pressure of chlorination, catalyst, etc. The kinetics of chlorination have been summarized by Groggins[10] into six major items. The unsaturated bond in the side chains generally gets chlorinated first. Nuclear substitution occurs[11] in the presence of halogen carriers such as iron, aluminium or iodine, usually at relatively low temperatures with the exclusion of light. The direct chlorination of phenol, normally at temperatures below 100°C. often in the presence of solvents such as carbon tetrachloride, sometimes in the presence of halogen carriers such as iron, aluminium chloride, leads primarily to substitution in ortho and para positions and later in meta position[12]. The rate of chlorination is favourably affected by the concentration of the molecules in the associating solvent[13].

The apparatus for chlorination[14] is usually of glass though quartz apparatus has been suggested, specially when ultraviolet light is used for catalizing the reaction. Henri[15] used an apparatus mainly of iron and lined with an insoluble halide such as calcium fluoride or silver chloride, at a temperature of 500 to 600°C. An apparatus for speeding the chlorination reaction by improved mixing has been reported by Kipper[16]. Application of the technique of the measurement of oxidation-reduction potential to control acid catalyst in the hydrochlorination has also been mentioned[17]. The principal chlorinating agent is gaseous chlorine alone (with light or heat as promoter) or in the presence of a catalyst. Other agents, such as hydrogen chloride, sulphuryl chloride, phosgene, hypochlorites, and thionyl chloride are used for the substitution of hydrogen, addition to the unsaturated linkages, and replacement of functional groups, such as hydroxyl groups in alcohols[9].

A Russian worker[18] discussed the mechanism of chlorination of organic and inorganic compounds by free chlorine and its derivatives in the presence of some inorganic chlorides as catalyst with or without the addition of carbon. The order of activity of the catalyst during chlorination of naphthalene is reported[19] as Sb $>$ Fe (powder) $>$ $AlCl_3$. Though the selection of a catalyst depends upon the nature of the reaction and the end-product required, the commonly used catalysts are Fe[20], Te[21] and its compounds, activated charcoal and chlorides of Te, Fe, Sn, Bi, Sb, Al[22] and P. Iodine in combination with iron has been reported to be a very powerful catalyst for organic compounds[23]. A mixture of sulphur, antimony chloride and lead has been successfully used as catalyst for the nuclear chlorination of benzene[24]. Bondy[25] suggested sulphuryl chloride as catalyst for chlorination of tar acids from l. t. tar.

Of all the isomeric forms of alkyl phenols and cresols, straight chain primary products are most active. A given number of carbon atoms in a single alkyl chain contributes[26] more activity than when distributed between two or more chains. The position[27] of alkyl groups with respect to hydroxyl group has little significance, e.g. ortho-, meta- or para-cresol, all have a Rideal Walker coefficient of 2·2. The germicidal activity increases against all organisms as alkyl chain is lengthened until the n-amyl compound is reached and thereafter further increase of the chain length results in decrease in activity against *salmonella typhi*. The effect on the gram positive organisms is uncertain[28]. The dihydrics of l.t. tar generally have[29] low antibacterial activity except hydroquinone (R. W. about 12). Suter[30] has stated, "The effect of halogen substitution, in general, increases with increasing atomic weight of the halogen" and "this increase is less for the ortho position than for the para, perhaps owing to interaction between the hydroxyl groups and the halogen atoms. Little evidence is available for meta compounds".

Chemically, the chlorophenols behave very much like phenols. The main differences[12] are the higher acidity as indicated by the ionization constant and the increase of bactericidal value as obtained from the phenol coefficient. Sixteen of the nineteen possible chlorophenols have been examined in an investigation into the relationship between chemical structure and germicidal activity[31]. From this it emerged that activity increased progressively to the trichloro derivatives, but decreased in the tetra- and penta-chloro series. The only reason advanced for the decrease was the limited solubilities of the compounds and higher *p*H values required for the solution.

EXPERIMENTAL

Materials. 1. Tar acid (boiling range 125 to 140°C. at 5 to 5·5 in. Hg, mainly a xylenol-cut fraction) was obtained by alkali extraction of l.t. tar oil followed by fractionation in a 80 lb. per batch capacity stainless steel unit. 2. Chlorine from commercial gas cylinders supplied by Messrs Mettur Chemicals Ltd., Mettur.

Procedure. Chlorine was passed through 500 g. of the tar acid fraction contained in a one litre, 4-necked glass flask, at a fairly constant rate at room temperature (30±1°C.) without any catalyst. Chlorine was passed through a sulphuric acid bubbler, a manometer and finally into the reaction flask. Excess chlorine along with the hydrogen chloride gas produced in the reaction was allowed to escape through a bubbler. In industrial practice excess chlorine after removal of the hydrogen chloride gas by absorption is compressed and reused. A stirrer was used continuously throughout the experiment and the gain in weight due to absorption of chlorine was recorded every two hours.

Five samples containing different per cent of chlorine were collected during the experiment. The samples were thoroughly washed with water to remove free HCl and Cl_2 and dried using ether as solvent. All these samples were studied for specific gravity, refractive index and colour of their emulsions.

RESULTS AND DISCUSSION

There was practically no further increase in weight after passing chlorine for 28 hr. If the increase in weight is assumed to be due to absorption of chlorine alone, the final product contained 59·47 per cent by weight of chlorine. The analyses of the different samples are given in Table 1.

Chlorinated samples 2, 3 and 4 were dark in colour, particularly No. 3, which had a dark magneta colour. The colour improved considerably with increase in chlorine content, the final sample No. 6 having only light orange colour. Towards the end of the reaction the quantity of excess chlorine increased and may have exerted bleaching action resulting in the light colour of the product. The emulsions from all the six samples gained colour after keeping for 24 hr. Maximum colour was again observed for sample No. 3 followed by 2. Raw tar acid fraction gave minimum colour to the emulsion.

Sample with 44 per cent by wt of chlorine deposited needle-shaped crystals. The crystals were washed, and recrystallized. The melting point of the crystals had a wide range of 70° to 92°C., the major portion melting between 88° and 92°C., and indicated mixed chlorinated tar acid products.

TABLE 1—ANALYSES OF THE CHLORINATED TAR ACIDS

No.	Details of sample	Cl_2 content (calculated) % by wt	Sp. gr. 30°C.	Refractive index 30°C.
1.	Tar acids fraction	..	1·003	1·529
2.	Chlorinated tar acid	10·07	1·047	*
3.	do	20·07	1·147	*
4.	do	44·73	1·396	*
5.	do	55·24	1·494	1·5653
6.	do	59·47	1·521	1·5583

*—Could not be determined due to dark colour of the product.

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Preparation of Disinfectant Grade Creosote from Low Temperature Tar

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A process to make white emulsion grade creosote from low temperature tar is described. All the tar fractions were found to impart colour to their emulsions. Air blowing at high temperatures for long duration in presence of catalysts (iron and its compounds or caustic soda) was found to give a white emulsion grade product. Treatment at higher pressures with or without use of ultraviolet light can be used advantageously to reduce the overall time of treatment.

One of the characteristic properties of a low temperature (l.t.) tar is its high content of tar acids of high bactericidal value. Bristow[1] reported that high-boiling tar acids (300-360°C.) from coalite tar have a Rideal Walker coefficient as high as 90. L.t. tar fractions or tar acid fractions therefrom are therefore ideally suited for the production of disinfectants and antiseptics. But they (particularly the phenolic constituents) gain red or brown colour in aqueous media, especially if the medium is alkaline[2]. Although the Indian Standard Specification does not mention[3] any criteria for the colour of the disinfectant emulsion, white emulsion-grade creosote is usually preferred by the user. The traditional source of this raw material in India has been high temperature or gasworks tar. The creosotes from l.t. tar, have thus a major drawback for their successful utilization in disinfectant manufacture. The removal of colour forming substances, therefore, assumes considerable practical importance in the successful utilization of l.t. tar.

The reason for the development of colour in emulsions from such tars have been studied by several workers. The important conclusions are summarized below:

(*a*) Colour formation is most marked in tars obtained from coal carbonized at temperatures 550-700°C.[4]

(*b*) Pink or red colouration is only due to polyhydric phenols[5].

(*c*) Substances responsible for red colour are not present as such in the tar fractions[2] but are produced only by the simultaneous oxidation in alkaline solution of homocatechol and derivatives of resorcinol[1]. Catechols alone do not give the red colour reaction[2,6]. Macleod[7] concluded that the coloured compounds resulted from a "benzenoid-quinonoid transformation with subsequent oxidation to a deeper coloured compound".

(*d*) Baker recorded the presence of a methyl group in the para position of a catechol as essential for the production of the typical red colour, though the nature of resorcinol was not critical. The most brilliant red colour was given by a mixture of 3 : 5 dimethyl catechol and 2 : 4 dimethyl resorcinol. 3-Methyl catechol and 3 : 6 dimethyl catechol were the only exceptions in the series and gave no red or orange colour with any of the alkyl resorcinols so far tested[6].

Literature on the extraction of polyhydrics from tar acids or tar oils is mostly covered by patents. Burke and coworkers[2] were probably the first to use a concentrated solution of borax to completely extract the colouring matter (C.M.) from the tar oils. In this process the tar oil was washed twice, each time with an equal volume of concentrated solution of borax, resulting in a product which gave white emulsion grade disinfectants. Another significant inference from his studies on distillation of C.M. is its probable distribution throughout the range of the tar oil. Macleod and coworkers made a detailed study of the problem and reported that (*i*) increase in concentration and proportion of caustic soda solution and number of treatments of creosote oil did not reduce the colour formation, (*ii*) use of hot or cold saturated solution of borax, or air blowing of sodium cresylate solution with or without addition of oxidizing agents met with only partial success, (*iii*) use of several types of reducing agents for retarding oxidation of colour forming substances gave good results, but had the objectionable feature of reducing agents remaining in the distillate. His final suggestion was blowing free oxygen-containing gas through sodium cresylate solution at as high a temperature as possible. The above processes are combined in a British Patent to Bondy and Tunnicliff[8] in which tar acids or tar fractions are first washed with an aqueous solution of boric acid or a borate and then oxidized by passing an oxygen-containing gas, followed by distillation to get white emulsion-grade creosote oil. Another U.S. Patent[9] described blowing free oxygen containing gas at elevated temperature through the aqueous alkali solution of high boiling tar acids and extracting the colour-forming bodies later with low-boiling hydrocarbons. According to a Japanese Patent[10], tar acids are oxidized in the liquid phase, with or without oxidizing agent, followed by air oxidation of the liquid and vapour phases. The distillate is later washed with aqueous sodium carbonate solution giving a product free of pyrocatechol. Another Japanese Patent[11] mentions recovery of catechol from a tar oil boiling below 260°C. by extracting with 1 per cent caustic soda solution, acidifying the extract and distilling. Williams[12] suggested the use of sodium bicarbonate for extraction of catechols from l.t. tar. Use of aqueous ammoniacal solution of calcium chloride to precipitate 3-methyl pyrocatechols from coal tar or peat tar is the subject of a Czech Patent[13]. In recent years aqueous methanol for removal of dihydrics has been suggested[14,15]. Zemplen and Dory[16] suggested the use of buffer solutions 3 per cent borax, 2 per cent sodium phosphate or 2 per cent sodium carbonate for extraction of catechols.

The object of present work was to develop a process by which the substances responsible for colour in l.t. tar creosote could be recovered or destroyed *in situ* so that the distilled product gives white emulsions which do not get discoloured on keeping. As the commercial cresylic creosote grade I[17] contains 90 per cent fraction boiling below 230°C., and as the fraction boiling up to 230°C. contained only a small percentage of polyhydrics, a process[19] to destroy them *in situ* is described briefly in this paper.

MATERIALS AND METHODS

L.t. light tar (LST-L) was obtained from the 25-ton per day capacity low temperature carbonization pilot plant operating at the Laboratory. A typical analysis of l.t. light tar and of l.t. cresylic creosote (LT/TD/C) obtained by distilling the tar in a 3-ton batch distillation pilot plant is given in Table 1.

Two commercial cresylic creosote samples, one from Government Industrial Testing Laboratory, Bangalore, and another from Messrs Standard Chemicals and Pharmaceuticals, Bombay, were obtained for comparative studies. Fraction up to 230°C. was about 70 per cent and contained 26-27 per cent by volume of alkali-soluble tar acids.

Castor oil soap was obtained by saponifying refined castor oil with caustic soda. The soap contained less than 0·5 per cent free alkali.

EXPERIMENTAL PROCEDURE

The l.t. creosote oil was mixed thoroughly with one or more of the catalysts mentioned in Table 3, heated to the required temperature, and air was passed at the rate of 0·5 cu. ft/lb. of charge/hr through the heated mixture for 2 to 4 hr. At the end of the period, air was stopped and distillation continued to get the white emulsion-grade disinfectant creosote oil. The laboratory experiments were done in a 4-neck Pyrex flask of 1 litre

TABLE 1—ANALYSIS OF TYPICAL SAMPLES OF LST-L AND LT-TD/C

	LST-L	LT-TD/C
Sp. gr. 30/30°C.	0·99	0·94
Alkali-soluble tar acids, vol. %	28·0	39·0
Distillation, vol. % (dry basis)		
Up to 210°C.	16·0	73·0
210-230°C.	18·0	24·0
230-250°C.	19·0	..
250-270°C.	13·0	..
270-290°C.	11·0	..
290-310°C.	10·5	..

capacity. An iso-mantle, wet gasmeter, manometer and a stirrer were the accessories used in the laboratory experiments. Based on the data obtained from the laboratory experiments, pilot plant experiment in the 3-ton batch unit having all necessary accessories were conducted and about 10 tons of white emulsion-grade disinfectant creosote were prepared.

COLOUR STUDIES

Five cubic centimeter of 25 per cent castor oil soap solution and 5 cc. of raw tar oil or the tar oil fraction (up to 230°C.) obtained by the standard distillation (as per STPTC) of the treated oil were taken in a 500 cc. measuring flask, mixed and diluted with distilled water up to the mark. After thorough mixing of the sample, about 25 per cent of the solution was discarded, and the flask with the remaining solution was loosely covered with paper and kept aside for 24 hr. At the end of the period, the colour of the solution was read using a Lovibond tintometer and a 1/4 in. cell.

Due to nonavailability of a suitable equipment to read the colour of the emulsions by reflected light, which would have been very near the visual observation, Lovibond tintometer which uses transmitted light for recording was used as a comparative measure. The unit gave the colour of the emulsions in terms of red, yellow and blue. Red units, though masked by blue to some extent, gave the general picture of the emulsion. The size of the emulsion particles also affected the final appearance by transmitting less light resulting in a higher blue reading. In general it was found that 0·4 to 0·5 units of blue as excess over red units gave a perfect white appearance of the emulsion.

RESULTS AND DISCUSSION

Though Currey[5] mentioned that when l.t. tar is properly fractionated oils boiling below 230°C. did not give coloration, in the present studies it was found, all fractions of l.t. tar contained the colour imparting substances (Table 2) 230-250°C fraction having the maximum followed closely by 250 to 270°C. fraction. These are in conformity with the findings of several other workers[1,2,6,18]. Studies of the commercial samples indicated that cresylic creosote from Bangalore alone was greyish white in colour; and the rest were coloured with different shades of pink.

Over hundred experiments were done; typical results are presented in Table 3. Fractions up to 230°C. from commercial samples (1 and 2) had a naphthalene smell indicating their origin from high temperature tar, and gave dense white emulsions. This may be due to bigger emulsion particles resulting in higher readings for blue, compensating for red and affecting the final appearance of the emulsions. Emulsions from l.t. tar creosotes, generally having red less than 4·3 and blue more than 4·7, gave perfect white emulsions. It is possible to improve further on blue counts by proper formulation resulting in dense and whiter emulsions.

Effects of temperature of air blowing (No. 4 to 6), duration of blowing (5 and 7), stirring (8 and 9), ultraviolet light (5 and 8), air blowing (11 and 13) and of different other catalysts (10 to 22) on the reduction of red colour of emulsions are presented in Table 3. Higher temperatures of air-blowing,

TABLE 2—TINTOMETER READINGS OF THE RAW SAMPLES

Sample details			Tintometer reading		
			Red	Yellow	Blue
Fraction up to	210 C.	from l.t. light tar	9·4	14·2	4·1
	210-230°C.	do	11·7	12·3	4·6
	230-250°C.	do	13·4	14·3	6·6
	250-270°C.	do	12·7	12·4	3·2
	270-290°C.	do	12·7	13·4	4·6
	290-310°C.	do	11·1	14·4	5·6
0-230°C. obtained from tar distillation pilot plant			9·3	13·2	5·1
Cresylic creosote (Bangalore)			7·6	15·4	8·4
Cresylic creosote (Bombay)			10·1	16·0	8·9
Blank (soap only)			0	0	0·1

TABLE 3—TINTOMETER STUDIES ON 0-230°C. FRACTION OF TREATED TAR OILS

DETAILS OF THE SAMPLE	TREATMENT				DISTILLATION IN TAR F_4 YIELD UP TO 230°C. (dry basis) vol. %	TINTOMETER READING		
	Temp., °C.	Air rate, cu. ft/lb./hr	Duration, hr	Catalyst, wt %		Red	Yellow	Blue
Cresylic creosote (Bombay)	..	..	..	..	61·1	5·1	11·0	6·4
Cresylic creosote (Bangalore)	..	..	..	..	70·5	5·1	11·2	6·2
LT-TD/C	..	..	..	..	96·0	7·1	13·4	4·8
do	100	0·5	2	..	96·5	6·8	12·5	4·6
do	150	0·5	2	..	94·5	6·6	11·6	4·7
do	185	0·5	2	..	94·0	4·3	9·2	4·6
do	150	0·5	2	..	92·0	4·5	9·8	4·8
do	150	0.5	2	U.V.	94·0	4·6	9·6	4·8
do*	150	0·5	2	,,	93·0	5·5	11·1	4·6
do	100	0·5	2	0·5% NaOH	95·0	4·5	9·7	4·6
do	150	0·5	2	,,	93·0	4·3	9·1	4·6
do	150	0·5	4	,,	90·0	4·1	9·1	4·5
do	150	..	2	,,	93·5	4·4	9·0	4·7
do	150	0·5	2	1·0% NaOH	89·5**	4·2	9·0	4·8
do	150	0·5	2	0·5% Fe dust	92·2	4·2	9·2	4·7
do	150	0·5	2	0·5% Fe_2O_3	93·0	4·1	8·7	4·6
do	150	0·5	2	0·5% $FeCl_3$	90·0	4·3	9·0	4·7
do	150	..	2	do	93·0	4·4	9·1	4·8
do	150	0·5	2	0·5% Conc. HNO_3	93·0	4·2	13·5	4·7
do	150	0·5	2	0·5% $AlCl_3$	92·0	4·9	11·2	4·8
do	150	0·5	2	0·5% $ZnCl_2$	93·0	4·3	8·7	4·8
do	150	0·5	2	0·5% $SnCl_2$	94·0	4·5	9·3	4·7

* Done in a quartz flask without stirring.
** Up to 226°C. only.

longer duration of stirring, ultraviolet light and use of catalysts resulted in the reduction of red colour of the emulsions.

It was not possible to blow air at a temperature higher than 185°C. mainly due to (*i*) commencement of distillation and (*ii*) frothing due to water formed during the reaction.

Best results were obtained by blowing air through the tar oil (LTTD/C) for 2 hr at 150°C. at a rate of 0·5 cu. ft/hr for 2 hours using 0·5 per cent ferric oxide as catalyst followed by distillation giving 4·1 red and 4·6 blue to the emulsion. Blowing air at 150°C. at the same rate for 4 hr and using 0·5 per cent sodium hydroxide also resulted in a product with 4·1 of red units. But the total yield of distillate up to 230°C. from the oil processed, was low (only 90 per cent), probably due to polymerization.

Sample No. 9 had marked yellow colour and this may be due to the presence of some nitrated compounds formed during the treatment using nitric acid as catalyst.

These experiments indicate that treatment at higher pressures with or without ultraviolet light can be used advantageously to reduce the overall time of treatment.

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DISCUSSION

Dr H. S. Rao: In our studies on colour removal from tar oils, low boiling tar oils which contain phenol only gave colour. Suspecting this to be due to the presence of iron as a result of corrosion in the plant, the tar oil was tested for iron by spectroscopic methods. No iron was found. There can be no polyhydric phenol in this cut and hence the question regarding the source of colour-forming bodies remains unanswered.

Shri D. P. Agrawal: The presence of colour-forming bodies in l.t. tar oils is known for quite some time. This subject was investigated as early as 1885. The colour-forming matter in l.t. tar oil was isolated and investigated by Baker in 1927. It was found that this material distils above 200°C. and the distillation range goes up to 262 C. L.t. tar contains complex materials and during standard distillation, they may form some azeotropes and some of the high boiling materials may go in the lower fractions. What exactly is the colour formation due to is not yet clear.

Dr S. K. Sircar: A figure of 90 has been reported for R.W. value of the l.t. tar acids from coalite tar. I am of the opinion that this figure is 56 and that too due to the presence of certain fractions of tar oils. Secondly what kind of emulsion was prepared and what was its *p*H ? The *p*H is very important. Was any microscopic examination of the emulsion done to detect any coalescence of particles on standing ? The colour is also influenced by the particle size.

Shri D. P. Agrawal: The figure for R.W. value of Coalite tar oils was given in the paper by Col. Bristow in the Journal of Institute of Fuel. During the discussion on the paper, he had explained as to how such a high value was obtained. G. Sykes in his book 'Disinfection and Sterilization' mentions about increase of germicidal activity as the alkyl length of the tar acid increases, n-amyl compounds having the maximum value.

The usual procedure for preparing emulsion was followed by us. The castor oil soap solution was made slightly alkaline before use. No *p*H measurements were taken. The particle size was not determined but this study is on our programme.

Shri M. C. Bakshi: The various points raised here are of special interest to the industry. High-boiling tar acids are not available in the country and these are being imported in large quantity. I would like to know whether Shri Agrawal has estimated the percentage loss of original tar acids after catalytic treatment and also the percentage tar acids in the distillate up to 230°C.

Shri D. P. Agrawal: There was practically no loss of tar acids observed after the catalytic treatment. The distillate up to 230°C. contained about 40 per cent tar acids.

Preparation of Electrode Binder Pitch from Low Temperature Tar

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Investigations have been carried out to increase the coking value of low temperature tar pitch to meet the specifications of electrode binder used for making carbon anodes for aluminium industry. On boiling a heavy tar fraction b.p. > 230°C. from low temperature tar with catalysts and subsequently distilling it or by processing low temperature tar pitch by methods such as treatment with sulphur, blending with high temperature tar pitch, etc. pitches of softening point 75° to 85°C. (R and B) were obtained which had a coking value near the specification requirement but their ash content was more than what is permissible.

Processing of low temperature (l. t.) tar into electrode binder pitch used for making carbon anodes required in aluminium industry has received attention only in recent years as one of the methods for the profitable utilization of the tar[1,2]. In the widely used Soderberg continuous process the carbon anodes used are of the self-baking type comprising of calcined petroleum coke or pitch coke bound with coal tar pitch. For every ton of aluminium produced the requirement of pitch is about 0·2 ton. The properties desired in the carbon anode are high mechanical strength and resistance to oxidation. Both these properties depend on the quality of pitch used as binder.

The commonly used criteria for assessing the quality of pitch binder are the softening point and coking value. The pitch should have a softening point low enough to permit easy handling and mixing with the coke grist. Its coking value should be high so that, besides forming a strong bond between coke particles, the pitch should itself give a high yield of coke during the process of baking to make the resulting anodes strong and dense. At present, only the pitch obtained from high temperature (h. t.) tar produced in coke ovens or gasworks is used for this purpose. On the other hand, l. t. tar pitches of the required softening point have low coking values, and are therefore considered unsuitable. This is attributed to their low aromaticity and high hydroxyl content[3]. Many processes such as treatment with condensing agents[4–6] treatment under high temperature and pressure followed by sudden cooling[7], etc. have been investigated and patented but all these pertain to h. t. tar pitch. Except for limited patented literature on severe thermal treatment[8,9], there is no information available on upgrading l. t. tar pitch for use as electrode binder. This paper describes the investigations conducted to find a simple method to increase the coking value of l. t. tar pitch to specification level without increasing its softening point.

MATERIALS AND METHODS

The heavy tar b.p. >230°C. was obtained from the 25 tons/day low temperature carbonization pilot plant operating at the Regional Research Laboratory. In this plant the tar is fractionally condensed into heavy and light tars. The l. t. pitches of softening point 83° and 127°C. were obtained from the 3 tons/day pot type tar distillation pilot plant operating at the Laboratory. The h. t. pitch of softening point 49°C. was obtained by distilling gasworks tar supplied by Messrs Bombay Gas Company. The properties of the heavy tar and pitch used are presented in Tables 1 and 1A. The coking value was determined by the method described by Charette and Bischoferger of Aluminium Laboratories, Canada[10].

The specifications of electrode pitch used by aluminium industries in India are presented in Table 2.

EXPERIMENTAL

Pitch Treatment Process

Blending with High Temperature Pitch. Fifty grams of l. t. pitch of softening point 127°C. and 50 g. of high temperature pitch were blended in a 3-necked flask of 250 ml. capacity fitted with a stirrer and thermometer and placed on a heating mantle. The temperature of the mixture was raised to 150°C. when it was completely molten.

The mixture was blended well by stirring for 1 hr at 150°C., and a sample of the blended pitch was then taken for determination of softening point and coking value. The results are presented in Table 3.

Treatment with Sulphur. Hundred grams l. t. tar pitch of softening point 83°C. was melted in the 250 cc. 3-necked flask. The temperature of the molten pitch was controlled at 150°C. and the required amount of sulphur was added in small quantities with continuous stirring over a period of 15 min. After addition of sulphur, the pitch was stirred for 1 hr at 150°C. A sample of treated pitch was then taken for determination of softening point and coking value. The results are given in Table 4.

TABLE 1—PROPERTIES OF HEAVY TAR FRACTION OF LOW TEMPERATURE TAR

Sp. gr. at 25°C./25°C.	1·07
Softening point, °C. (ring and ball)	28-30
Insoluble matter in toluene, wt %	1-1·2
Distillation data	
Initial boiling point	240°C.
Fraction up to 300°C., wt %	3-4
300°-360°C., wt %	32-35
Residual pitch above 360°C., wt %	60-62
Coking value, wt %	7

TABLE 1A—PROPERTIES OF PITCH

	Softening point, °C. (R & B)	Coking value, wt %	Ash, wt %
L.t. pitch from pilot plant	127	46·62	0·79
L.t. pitch from pilot plant	83	34·3	0·40
H.t. pitch (gasworks)	49	36·26	0·78

TABLE 2—SPECIFICATION OF ELECTRODE PITCH USED BY ALUMINIUM INDUSTRIES IN INDIA

	Aluminium Corporation of India	Indian Aluminium Co. Ltd.
Softening point, °C.	70-78 (Kraemer and Sarnow)	63-70 (Cube-in-water)
Coking value, wt %	Not less than 48	Not less than 50
Ash, wt %	Not more than 0·3	Not more than 0·3

TABLE 3—EFFECT OF BLENDING WITH HIGH TEMPERATURE TAR PITCH

	Softening point, °C. (R & B)	Coking value, wt %	Ash, wt %
L.t. tar pitch from pilot plant	127	46·62	0·79
H.t. tar pitch (gas works)	49	36·26	0·78
Blend of 1 and 2 in the proportion of 1:1	86·75	42·66	0·78

TABLE 4—EFFECT OF TREATING LOW TEMPERATURE TAR PITCH WITH SULPHUR

	Softening point, °C. (R & B)	Coking value, wt %	Ash, wt %
L.t. tar pitch from pilot plant	83·0	34·3	0·40
No. 1 treated with 5% sulphur	82·25	39·16	0·40
No. 1 treated with 10% sulphur	77·63	42·14	0·34
No. 1 treated with 15% sulphur	73·37	45·09	0·25
No. 1 treated with 20% sulphur	73·5	48·65	0·28

Treatment of Heavy Tar with Catalysts. Hundred grams heavy tar containing the required amount of added catalyst was boiled at 340-350°C. for 5 hr in a 150 ml. flask fitted with a thermometer and condenser. After this treatment the tar was distilled to a pitch of softening point 75-90°C. A sample of the pitch was taken for determination of softening point and coking value. The results are given in Table 5.

DISCUSSION

From Table 3 it is seen that the coking value of the blended pitch is only 8 per cent less than the specification. The gasworks tar pitch used for blending appears to be of an inferior quality because its coking value is lower than that of an average sample. The coking value of the blended pitch could be increased to specification level if a good quality h. t. pitch is used.

Table 4 shows that the increase in the coking value of treated pitch is nearly equivalent to the amount (per cent by wt) of sulphur added. Addition of 15 per cent by wt of sulphur increased the coking value to 47 per cent, with a significant decrease in the softening point. During the addition of sulphur an increase in the fluidity of the pitch was observed and a small amount of hydrogen sulphide was evolved. According to Krylov[11] the action of sulphur on pitch cannot be explained only in terms of the fusion diagram but the sulphur reacts chemically with the pitch by combining at the double bonds between the carbon atoms in the following manner:

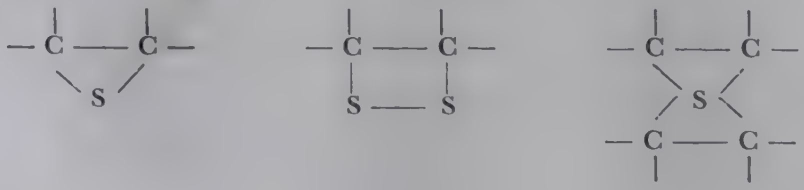

TABLE 5—EFFECT OF TREATING LOW TEMPERATURE TAR WITH CATALYSTS

	SOFTENING POINT, °C.	COKING VALUE, wt %	ASH, wt %
Heavy tar pitch	74·5	27·43	0·12
Heavy tar boiled with 1 wt % of tin powder	82·5	36·89	0·28
Heavy tar boiled with 1 wt % stannous chloride	87·0	44·11	1·62
Heavy tar boiled with 1 wt % zinc powder	73·0	38·19	1·08
Heavy tar boiled with 1 wt % zinc chloride	75·0	36·59	0·82

It is likely that part of the sulphur added remains behind in the coke and may contribute to the increased coking value of pitch. Although the specification for electrode binder pitch does not mention about the sulphur content it is not known whether such a high percentage of sulphur is tolerable. However, it has been claimed that the gas yield during coking of sulphur-treated pitch is one-fourth of that from untreated pitch[11] and that petroleum coke containing as much as 6 per cent of sulphur could be used for the production of aluminium without deleterious effects[12].

From Table 5 it is seen that of the catalysts tried stannous chloride ($SnCl_2 . 2H_2O$) appears to be the best. Treatment with even 0·5 per cent by wt of $SnCl_2$ increases the coking value by 12 per cent. On using 1 per cent $SnCl_2$ the coking value is increased to 42 per cent which is only 8 per cent less than the specification requirement but its ash content is 1·62 per cent which is beyond the limit. The disadvantage in using such inorganic catalysts is that they add to the ash content of pitch necessitating further treatment of pitch to reduce its ash content.

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Low Temperature Tar: A Raw Material for Production of Low Ash Carbons

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Low-ash carbon is one of the essential basic raw materials for electrometallurgical and electrothermal industries. In this review the position in India regarding the present and future availability of body materials like petroleum coke, anthracite and pitch coke required for low-ash carbon manufacture is examined and the need for exploring additional sources for this purpose is stressed. The possibility of profitable utilization of low temperature tar pitch by converting it into coke for electrodes is discussed and a brief account is given of the work in progress at the Regional Research Laboratory, Hyderabad.

Low-ash carbon is one of the essential basic raw materials for electrometallurgical and electrothermal industries. It is employed in the form of electrodes, as a reducing agent in nonferrous metallurgy especially in the production of aluminium, as a chemical reactant in the manufacture of calcium carbide, silicon carbide, carbon disulphide, etc. and as a material of construction and as heat conductor in industries producing furnaces, motor brushes, arc carbons, etc. By the end of the Third Five Year Plan the requirement of electrode carbon by the Indian Aluminium Industry alone is expected to be about 45,000 tons per year. Special types of carbon in the form of brushes and arc carbon are still imported and the value of such imported carbons was more than 10 million of rupees in 1957.

The raw materials for low-ash carbon manufacture may be divided into two classes: (1) Body materials, which are the carbonaceous materials making up the bulk of the finished article, (2) binders, which serve to hold together the finely ground particles of the body materials. In this review, the present position regarding the availability of body materials in India will be considered.

SOURCES OF BODY MATERIALS

Petroleum Coke. This is the most widely used body material. In the U.S.A. it is produced to the extent of more than a million tons per year. It is obtained as a residue from petroleum refining operations such as thermal cracking or delayed or fluid coking. At present it is produced in India only by the Assam Oil Co. at Digboi Refinery. It has a high silicon content and is, therefore, reported to be not acceptable by the aluminium industry for the production of conductor grade metal which forms the major outlet for aluminium[1,2]. Since the two refineries proposed to be set up in the public sector at Nunmati and Barauni are also based on the same Assam crudes, the petroleum coke to be produced by them may not be expected to be of the desired quality. Furthermore, advances in petroleum technology constantly aim at reducing coke production and to get more of the distillates for which the demand is high. So, if a suitable substitute for petroleum coke is made available it will help in reducing the present shortage of distillates to some extent.

Anthracite. Good quality anthracite suitable for electrode manufacture is not available in India. Only semi-anthracite with a volatile matter content of 13 per cent and a high ash content of 16 per cent is available in Kashmir State. Devolatilizing and de-ashing of the semi-anthracite for subsequent use and its transport over necessarily long distances may not be economical.

Superclean Coal. The production of ashless coal by extraction of coal with tar oils at high temperature and pressure is still in experimental stage and studies are yet to be conducted to assess the commercial possibilities of the process.

Pitch Coke. Pitch coke is produced by destructive distillation of coal tar pitch in modified coke ovens or specially designed retorts. It has low ash and high fixed carbon contents and has much the same qualities as petroleum coke and can replace it wherever it is used. As the supply of petroleum coke continues to decrease due to changed methods of refining, its place will necessarily be filled by pitch coke.

Coke from high temperature (h.t.) tar pitch is the main body material used for low-ash carbon manufacture in U.S.S.R. and Germany. No pitch coke industry exists in India now but the future commercial production of coke from h.t. tar pitch may have the following limitations.

1. Owing to various reasons such as shortage of fuel oil, ready availability of tar, etc. a major portion of the h.t. tar produced by coke ovens attached to steel factories will continue to be used as fuel in the steel plants themselves.

2. Out of the pitch obtained from the tar distilled, the bulk of it would be used for production of road tar, electrode binder, roofing felt, etc. for which the demand will continue to rise as a result of the proposed expansion in highways, aluminium and roofing felt industries.

3. Since the reserves of high quality coking coals suitable for metallurgical coke production are limited, technological advances such as use of pressures and/or oxygen are likely to be adopted in blast furnace operation to reduce the consumption of coke per unit of pig iron produced. As a result of this the amount of h.t. tar produced by coke ovens may not increase further in future because the amount of metallurgical coke produced, by and large, also controls the amount of tar produced. Furthermore, if the processes being developed for direct reduction of iron ore using hydrogen happen to be adopted in future, they may seriously affect the production of h.t. tar.

Pitch Coke from Low Temperature Tar. From the above considerations, it is clear that it is necessary to explore additional sources of low-ash coke. Such a source can be the low temperature (l.t.) tar which will be produced in large quantities from the commercial low temperature carbonization (l.t.c.) plants expected to be set up in the near future for manufacture of domestic coke. Since pitch forms a major constituent of l.t. tar its effective utilization is very important. Investigations conducted in other countries, have clearly shown that converting the pitch to low-ash coke would be a convenient method for its profitable utilization.

INVESTIGATIONS CONDUCTED IN OTHER COUNTRIES

Production of electrode coke from l.t. pitch formed one of the main methods of its utilization in Germany during the Second World War when more than 25,000 tons of it were produced annually from l.t. pitch alone[3].

It was reported that a lignite carbonizing plant at Rositz in East Germany was building a cracking unit to process 90,000 tons of lignite tar per year along with 80,000 tons of press oils to obtain motor fuels and coke[4].

The industrial treatment of l.t. pitch in Poland consists of distilling the pitch to get coke for electrodes and heavy oil for boiler fuel[5].

In U.S.A. where almost the entire low-ash coke requirements are derived from petroleum coke, serious attention is being paid to the future production of coke from l.t. tar because of the likely shortage of petroleum coke as a result of improved refining techniques. For instance, the Pittsburgh Consolidation Coal Company, which is at present the foremost in the field of l.t.c. have operated a plant for coking the tar from the Disco Process. The company has also plans to establish a 2·5 million tons/year l.t.c. plant at Cresap, W. Va. The pitch from this plant is proposed to be used for production of electrode coke. The 'green' coke from the pitch coking stills is said to have a favourably low vanadium content and to give a dense, hard electrode coke on calcining[6].

At Rockdale, Texas, where a single large-scale prototype fluidized carbonizer is now undergoing tests, it is planned to use the residue from tar distillation for the production of electrode carbon[7].

Lummus Co. have successfully run l.t. tars through a pilot delayed coking unit to make gasoline and coke. Plans for a commercial venture are said to be in the making[4].

Alcoa Research Laboratories of Aluminium Company of America have conducted pilot plant tests on delayed coking of lignite tar. Compared with a petroleum feed, greater amounts of a less graphitic and tougher coke were obtained. The liquid products obtained in the process contained valuable low-boiling phenols[8].

In working out the economics of a projected 8,520 tons per day fluidized l.t.c. plant, Minet and coworkers[9] of United Engineers and Constructors Co., Pennsylvania State, that if the l.t. tar pitch is converted into electrode coke the returns would be 4 times its value as fuel and would make the overall economics of an l.t.c.-Aluminium or l.t.c.-Calcium Carbide Combination Plant very attractive.

INVESTIGATIONS AT THE REGIONAL RESEARCH LABORATORY, HYDERABAD

Investigations have been in progress at this Laboratory on the production of coke from l.t. tar produced from the 25 tons/day Lurgi-Spuelgas pilot plant operating at the Laboratory. The two methods tried for producing coke were: (1) Carbonization of hard pitch, and (2) pressure distillation of a heavy tar fraction (b.p. >260°C., 60 per cent by wt residue above 360°C.).

TABLE 1—ANALYSIS OF GREEN PETROLEUM COKE AND LOW TEMPERATURE PITCH COKES

	Commercial 'green' petroleum coke from delayed coker	Pitch coke by carbonization of hard l.t. pitch	Pitch coke by pressure distillation of heavy tar
Moisture, wt %	5—7	1·9	3·6
Volatile matter, wt %	9—12	9·7	14·4
Fixed carbon, wt %	84—90	86·4	80·3
Ash, wt %	0·3	2·0	1·7
Yield (% wt of heavy tar)	—	28·0	50·0

Carbonization of Hard Pitch. A hard pitch of softening point 127°C. (R & B) obtained by distilling heavy tar in the 3 tons/batch pot type tar distillation plant, was carbonized at 600°C. in the 2 kg. capacity Fischer-Schraeder retort.

Pressure Distillation of Heavy Tar. The heavy tar fraction (b.p. >260°C., 60 per cent residue above 360°C.) was distilled at 200 lb./sq. in. pressure in a 1-litre pressure distillation unit.

The yields and analysis of 'green' pitch cokes obtained during several tests are summarized in Table 1 and compared with commercial 'green' petroleum coke.

The ash content of the pitch cokes is somewhat higher. This may be due to the dust content of the tar which was not clarified before processing and contamination by metallic iron when the tar was distilled in the mild steel still. It should be possible to reduce the ash content of the coke to less than 0·5 per cent by preliminary treatment of the tar, as is done in Poland[10] and by using corrosion-resistant equipment for distillation. Investigations are in progress in this direction to obtain coke of lower volatile matter and ash contents.

CONCLUSION

In view of the present unsatisfactory position regarding the availability of 'body' materials for low ash carbon manufacture, serious consideration should be given to the possibility of producing pitch coke from the large quantities of l.t. pitch expected to be produced from the projected commercial l.t.c. plants. In addition to being a convenient method for profitable disposal, the processing of l.t. pitch to electrode coke would help in supplementing the requirements of low-ash coke and also yielding more liquid products which can be used as wood preservatives or processed to liquid fuels and chemicals.

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Suitability of Low Temperature Tar as a Road Binder for Black Top Surfacing

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Low temperature tar can be processed into a road binder by a simple process and the binder compares well with conventional binders in their engineering properties. A semi-field test track using this binder has been laid and is under observation. The chemical and physical properties of low temperature tar/pitch, methods adopted to process it into road binder and the properties of binder are also described.

The development of low temperature carbonization (l.t.c.) process is of comparatively recent origin and probably had its inception in Europe for the production of smokeless fuel for space heating since it is easily ignitable and readily combustible.

According to the available statistics[1] the production of low temperature (l.t.) tar in U.S.A. in 1952 was about 0·7 per cent of the total tar produced, the production in U.K. being somewhat larger. In Germany the production of l.t. tar is higher than any other country employing a low-grade coal (brown coal).

The tar yield is higher and is highly paraffinic in nature with a very low aromatic content. Its tar acid content is considerably higher than that in high temperature tar consisting mainly of high boiling tar acids.

No ready market has been developed for l. t. tar except as a fuel oil. In some countries in Europe, due to shortage of petroleum fuel resources the tar has been processed into motor fuel by hydrogenation. Byproduct recovery for l. t. c. has not been thoroughly worked out as in the case of the high temperature process. In the Disco process[2] the tar is directly sent to a tar still, where it is separated into the following products: road tars, crude tar and oil, disinfectant oils, floatation oils, creosote oil (wood preservative), tar paints, roofing and fuel pitches.

It is estimated that by 1970, roughly 5 million tons of l. t. tar will be produced annually as a byproduct from l. t. c. If this tar could be profitably disposed off, the economics of the l. t. c. industry can be by far improved.

Among the numerous uses of l. t. tar and its products, their use as road tar is probably of special importance, since it is processed only from the residual pitch leaving free the oils for other uses.

Due to the extensive road construction programme as envisaged in the Third Five Year Plan, the requirement of road binder will rise considerably. The quantity of road binders, both bituminous and high temperature (h. t.) tar types, produced in this country, may not be enough to meet the demand. L. t. pitch if processed to road tar can meet a part of the deficit.

With this object in view work on the processing of l. t. tar into road binder was undertaken by the Central Road Research Institute (CRRI), at the instance of Regional Research Laboratory (RRL), Hyderabad, where an l. t. c. plant is operating.

CHEMICAL NATURE OF L.T. TAR

L. t. tars are brownish oily liquids much thinner in consistency than h. t. tars. They consist of 50-80 per cent of hydrocarbons and 20-50 per cent of tar acids and according to Vahrman[3] l. t. tars produced at a carbonization temperature of 450-600°C. by external heating of the charge have the following characteristics:

(*a*) Hydrocarbons present are mainly naphthenic, paraffinic and alkylated-aromatic in structure.

(*b*) Alkylated hydrocarbons and phenols are predominant. The simplest phenol itself is virtually absent but the higher phenols like the cresols and xylenols, are in abundance. Polyhydroxy phenols such as catechol and resorcinol are also present.

(*c*) A large proportion of amorphous or resinous substance of various chemical types is present, for example, resinous phenols, resinous acids, resinous amines and resinous neutral compounds. They are soluble in benzene but not in light petroleum ether. Only a small amount of benzene-insoluble amorphous material is present.

PHYSICAL NATURE OF L. T. TAR AND PITCHES

Some general points of similarity have been observed between l. t. tar and crude petroleum[4] with regard to optical activity, high content of hydrogen and low specific gravity. The high-boiling fractions are paraffins and not anthracenes as in the case of h. t. tars, the phenol and free carbon content is low and naphthalene is present only in traces.

The base pitch for the production of road binder is usually obtained by straight distillation of the l. t. crude. The yield of pitch mainly depends on the viscosity of the dehydrated crude but generally a yield between 30-60 per cent is obtainable at a vapour temperature of 325°C. Pitches from l. t. tar differ considerably from those from h. t. tar both in the chemical and physical properties since the former contain more phenolic bodies, solid paraffins, and they are also low in specific gravity and free carbon content.

Engineering properties of the pitch from l. t. tars have not been fully investigated as in the case of h. t. pitches. A few references available in this field refer to only the laboratory findings. Binding and elastic property of l. t. tar have been investigated by Frankland Taylor[5]. The binding strengths of pitches from horizontal retort h. t. tar, vertical retort h. t. tar and l. t. tar were determined by them to be:

Horizontal retort h. t. pitch	400-500 lb.
Vertical retort h. t. pitch	300 lb.
L. t. pitch	200 lb.

The elasticity recoil of the pitches (in degrees of arc at the twist point temperature) are given below:

Horizontal retort and vertical retort h. t. pitch	3-15°
L. t. tar pitch	18°
Coke-oven tar pitch	20°
Blast-furnace pitch	30°
Petroleum bitumen	120-130°

This shows that the l. t. tar pitch compares favourably with coke oven tar regarding elastic recovery though the binding power is somewhat less. Further investigation by Wasserfuhr on lignite-tar pitch showed that its binding property is of the same order as that of coal tar pitch[6].

Oxidation resistance measured by rise in softening point of the various binders has been determined by Franck[7]. It has been found by him that h. t. coke oven tar is more resistant than vertical retort tar which in turn is more resistant than l. t. tar.

WORK DONE IN OTHER COUNTRIES

There appear to be quite a few processes developed for the production of road binders and allied substances from l. t. coal tar and lignite tar in other countries. The following are some of the processes reported: (*a*) Blowing of l. t. tar (lignite tar) with air in presence of mineral substances[8], (*b*) Blowing of a mixture of l. t. tar (lignite tar) and refined Trinidad asphalt[9], (*c*) Treatment of l. t. tar with lime[10], (*d*) Crude tar containing wax treated with sulphuric acid at 50-80°C.[11], (*e*) Treatment of crude tar with zinc chloride[12], (*f*) Autoclaving l. t. tar or its fractions above 300°C. with 'steel wool' at 320°C.[13], (*g*) Distillation of l. t. tar in presence of metallic zinc or aluminium so as to produce a residue having the properties of petroleum tar[14], (*h*) Cracked l. t. brown coal tar pitch of 72°C. (K & S) softening point[6] or less and blending with tar oils to the required viscosity of road binder, (*i*) Blending Disco tar pitch with Disco tar oil[15], (*j*) Distillation of l. t. tar in presence of Sodium hydroxide[16], (*k*) Low paraffin cracked pitch fluxed with dephenolated brown coal tar oil[17].

WORK CARRIED OUT AT CRRI AND RRL

For the production of base pitch for road binders, the crude tar is usually distilled. Alternatively, the tar can be thickened to a suitable pitch consistency by blowing air at elevated temperature. The next step for the production of road binder is to flux it back with suitable oil to the consistencies of different standard grades. For the production of base pitch from l. t. tar three different methods were adopted:

(1) Preparation of base pitch by air-blowing at elevated temperature, with or without a catalyst;

(2) Preparation of base pitch by straight distillation;

(3) Preparation of base pitch by mixing l. t. tar pitch of suitable softening point with a hard grade petroleum bitumen.

The first method was developed successfully by RRL for producing road tar by fluxing a pitch produced by air blowing with l. t. tar oil of suitable boiling range[18]. M/s Lurgi in Germany, have produced road binder from Indian l. t. tar and according to an unpublished report the road behaviour of the tars produced by them was satisfactory in the test-tracks[19].

In the CRRI, the base pitch was produced by the second and third methods. Dehydrated crude was straight distilled to soft and medium soft pitches having softening points of 60° and 75°C. R & B respectively. The pitch with a softening point of 60°C. was mixed with an equal amount of 10/20 pen. petroleum bitumen at a temperature of 125-130°C. by mechanical stirring. A stable mixture was formed, which, when further fluxed with tar oil to 80/100 penetration showed no separation of the components even on storage at 165°C. for 100 hr.

In the second method adopted by CRRI, the medium soft pitch of 75°C. (R & B) softening point, was fluxed back to the consistency of RT-4 as laid down by I. S. I., with tar oil. Tar oil in both the cases was high temperature anthracene oil (also known as heavy creosote oil) having the distillation ranges presented in Table 1.

Anthracene oil was selected as a fluxing oil because: (*a*) It is a good flux both for tar and bitumen, (*b*) It is nearly free from solid hydrocarbons like naphthalene and anthracene, (*c*) Due to its high boiling point, loss due

TABLE 1—DISTILLATION RANGE OF HEAVY CREOSOTE OIL

TEMP., °C.	WT %
Up to 200	1·5
200-270	30·4
270-300	14·3
300-340	22·7
340-350	5·9
350-360	7·0
Residue at 360°C. (EVT-24°C.)	18·2

to evaporation during heating as well as on the road is minimum, (*d*) Phenol content is negligible, and (*e*) Fraction up to 27°C. is sufficient to give a good setting property of the tar.

Tar/bitumen mix was fluxed to the consistency of a bituminous road binder since this mixture was expected to behave more like a bituminous binder than tar. Investigations of Tingle and Wright[20] and Macht[21] have shown that a mix containing 60 per cent of tar pitch and 40 per cent of petroleum bitumen behaved like the pure bituminous component in its temperature susceptibility and penetration index.

The binders used are (*a*) 80/100 pen. bitumen, (*b*) RT-4, (*c*) CRRI l. t. road binder processed to RT-4, (*d*) CRRI tar/bitumen mix equivalent to 80/100 pen., and (*e*) a l. t. road tar, equivalent to RT-4 processed by RRL, Hyderabad.

LABORATORY INVESTIGATION OF PROPERTIES OF BINDERS PROCESSED OUT OF L. T. TAR FOR THE TEST TRACK CONSTRUCTION

A systematic study of the properties of the binders prepared from l. t. tar was made to ascertain their suitability in engineering constructional works. The properties of these binders are compared with those of the standard conventional binders, both bituminous and tar types, in Tables 2 and 3.

Oven oxidation test was carried out to ascertain the oxidation susceptibility and setting properties. The tests were carried out at 115°C. for 2 hr and gases (nitrogen for evaporation change and oxygen for oxidation change) were circulated at the rate of 2 litres/min. The changes in softening points (R & B) are given in Table 4.

TABLE 2—BITUMINOUS TYPE BINDERS

Tests	Tar/bit. mix.	80/100 Bit.
1. Penetration at 25°C.	91	98
2. Sp. gr. at 27°C.	1·08	1·03
3. Softening point (R & B), °C.	49·5	47·2
4. Ductility at 27°C.	20* cm.	Over 100 cm.
5. Loss on heating, % by wt	3·0**	0·11
6. Penetration of residue due to loss of heating expressed as % of test (1)	40·00	92·00

*Very low.
**Fluxing oil is more volatile and is more liable for hardening during storage and mixing.

TABLE 3—PROPERTIES OF THE TAR BINDERS

	High temp. RT-4	CRRI LT-4	RRL-4	Limits of ISI for RT-4 grade tar
1. Sp. gr. (27/27°C.)	1·24	1·12	1·10	1·18-1·28
2. E.V.T., °C.	54·5	54·0	53·5	53-57
3. Flow time. B.R.T.A. viscometer (10 mm. cup) at 55°C. in secs.	43	47	46	40-60
4. Water content, wt %	0·1	0·2	0·2	Max. 0·5
5. Distillation, wt %				
Up to 200°C.	0·1	0·46	0·71*	Max. 0·5
200-270°C.	5·0	4·03	1·42	0·5-4
270-300°C.	4·1	5·49	17·69**	2-7
6. Softening point of the residue, °C.	57·3	53·7	54·8	Max. 54·0
7. Phenols, % in the fraction up to 270°C. (on whole tar), vol. %	0·2	0·4	0·49	Max. 2·0
8. Naphthalene, wt %	1·7	Nil	Nil	Max. 2·5
9. Toluene insoluble matter, wt %	16·9	8·8	4·14	Max. 24

*Above the specification.
**Much above the specification.

Since two hours exposure to oxygen at 115°C. was not conclusive about the oxidation behaviour of the binders, accelerated pressure oxidation test under a pressure of 300 lb./sq. in. of oxygen at 60°C. for 65 hr was carried out. Results of this oxidation test are given in Table 5.

TABLE 4—OXIDATION TESTS OF PITCHES

BINDER	SOFTENING POINT (R & B) BEFORE TEST, °C.	SOFTENING POINT AFTER 2 HR PASSING OF NITROGEN, °C.	CHANGE IN SOFTENING POINT (R & B) (A), °C.	SOFTENING POINT (R & B) AFTER 2 HR PASSING OF OXYGEN, °C.	CHANGE IN SOFTENING POINT (R & B) (B), °C.	CHANGE DUE TO OXIDATION B—A
Standard RT-4	35·8	40	+4·2	42·4	+6·6	2·4
RRL-4	38·8	40·8	+2·0*	42·8	+4·0	2·0
CRRI-4	38·8	42·0	+3·2	43·0	+4·2	1·0
80/100 bit.	47·2	47·8	+0·6	48·2	+1·0	0·4
Tar/bit. mix.	49·4	56·0	+6·6**	57·6	+8·2	1·6

*Slow setting. **Quick setting.

TABLE 5—ACCELERATED PRESSURE OXIDATION TESTS OF PITCHES

MATERIAL TESTED	SOFTENING POINT (R & B) BEFORE OXIDATION, °C.	SOFTENING POINT (R & B) AFTER OXIDATION, °C.	DIFFERENCE IN SOFTENING POINTS
RT-4	35·8	46·4	+10·6
RRL-4	38·8	66·2	+27·4
CRRI-4	38·8	65·6	+26·8
80/100 pen. bitumen	47·2	54·4	+ 7·2
Tar/bit. mix. of 91 pen.	49·4	69·8	+20·4

Results show that l. t. tar binders are more susceptible to oxidation than h. t. RT-4 and straight-run bitumen like 80/100 under very severe conditions.

Temperature susceptibilities of the l. t. tar binders were determined according to the formula of Mitchell and Lee, and were compared with that of 80/100 bit. & RT-4 (Table 6).

Adhesion characteristics of the binders were determined and compared with the standard binder. Four different types of stone were selected for the test including two granites which possess good stripping properties. The test was carried out according to the standard static immersion procedure developed by the Central Road Research Institute. The results are presented in Table 7.

The behaviour of l. t. tar binder in hot-mix hot-laid dense concrete constructions was also investigated in the laboratory. Flow and stability of the mixes were determined by Marshall Stability testing procedure[22] and the mix. was graded according to the specification A-2-b laid down by the Asphalt Institute. The results obtained are shown in Table 8.

Since 5·5 per cent of 80/100 binder is the optimum binder for this grading, the other binders besides 80/100 bitumen were kept in the same level in order to compare their stability values.

TABLE 6—LOGARITHIMIC TEMPERATURE COEFFICIENT* OF THE BINDERS

Temp. of determination	40°C.	50°C.	60°C.	70°C.	Log. temp. coeff.*
Viscosity of RT-4 in poises	8,510	..	880	..	7·64(a)
Viscosity of RRL-4 in poises	7,675	..	433	..	9·66(a)*†
Viscosity of CRRI-4 in poises	9,300	..	1,023	..	7·42(a)
Viscosity of 80/100 pen. bitumen in poises (actual pen. at 25°C.-98).	..	13,000	..	2,058	7·13(b)
Viscosity of tar/bit. mix. in poises (actual pen. at 25°C.-91)	..	11,900	..	1,880	7·12(b)

*Logarithimic temperature coefficients were calculated according to formula of Mitchell and Lee[23].

†More susceptible to temperature change than the other two binders of the series

(a) Between 40 and 60°C. (b) Between 50 and 70°C.

TABLE 7—ADHESION PROPERTY ACCORDING TO STATIC IMMERSION TEST % OF STRIPPED AREA

Rocky material	RT-4	CRRI-4	RRL-4	80/100 Bit.	Tar/Bit. mix.
Trap	nil	nil	nil	nil	nil
Delhi quartzite, %	nil	nil	30	nil	nil
Coarse-grained granite No. 1, %	5	nil	50	30	nil
Coarse-grained granite No. 2, %	20	15	75	25	nil

TABLE 8—FLOW AND STABILITY OF MIXES

Binders	% of binder on aggregate	Marshall stability lb. at 140°F.	Flow value in.	Voids %
80/100 pen. bitumen (pen. 98)	5·5	1593	0·15	4·0
Tar/bitumen mix. (pen. 91)	5·5	1918	0·18	5·4
RT-4 (EVT-54°C.)	5·5	868	0·11	7·6
CRRI-4 (EVT-54°C.)	5·5	1055	0·17	5·4
RRL-4 (EVT-53°C.)	5·5	992	0·17	4·0

Stability figures are quite good for a dense-mix construction and is generally much above the value recommended[22] for a tyre pressure up to 100 p.s.i.

TEST TRACK CONSTRUCTION

A test-track was constructed on the Delhi-Mathura Road in front of the CRRI during May 1961. The test-track carried an average traffic load of 5,000 tons a day and 90 per cent of it were heavily loaded trucks carrying building materials and goods. The road was opened to traffic in about twenty days after the construction of all the stretches was over. Before the actual test-track construction, the road was brought to proper level and cambre by laying a levelling course over the old road surface. Both surface dressing and premix carpet were laid for each binder according to the specifications laid down by C.P.W.D. Since the construction was carried by manual labour, rigid quality control was maintained throughout the work, except for one specification with CRRI-4, where the aggregates got over-heated due to a defect in the mixing plant. Length of each specification varied between 50-80 ft with a width of 22 ft.

CONSTRUCTION DETAILS

Specifications for Surface Dressing Work. About 35 lb. of binder were sprayed over 100 sq. ft area of the road and blinded with 5 cu.ft of 0·5 in. Delhi quartzite stone; for 80/100 bitumen the binder was heated to 150-160°C., for tar/bitumen mixture to 120-125°C. and for RT-4 and L-T-4's to 110-120°C. before application.

Specification for Premix Carpets. Forty lb. of hot binder was mixed with 8 cu. ft of 0·5 in Delhi quartzite stones in pre-heated stage and the mix was spread over 100 sq. ft area. For bituminous binders like 80/100 and tar/bitumen mix, the binders were heated to about 120-130°C. before mixing with the stones in a pugmill. The hot premix was uniformly spread over by means of rakes and spades and levelled uniformly by drag broom. The laid mix was rolled hot and finally covered with a seal coat consisting of 3 cu. ft of 0·25 in. grit with 15 lb. of the same binder and rolled again. Heating and mixing of the binder was carried out in a spot mix.

In the case of tar type binder like RT-4, CRRI-4, and RRL-4, the binders were heated to about 110-120°C. and then mixed with hot aggregates also at the same temperature.

Rolling in both the types of construction was carried out by means of a 8-ton three wheeler.

The test-track has been under observation for the last three months including a month of exceptionally heavy rain. Surface dressed with RRL-4, CRRI-4, and tar/bitumen mix are in very good shape. As for the single sized premixes with seal coat, though a few spots are showing signs of distress the surfaces on the whole are behaving satisfactorily. However, it is too early for any final assessment.

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Hydrogenation of Coal Tars and Possibilities of Producing Middle Distillates

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A historical account of the various stages in the development of hydrogenation of coal and coal tars is given. Hydro-treating as practised in the petroleum industry is described and the possibilities of using this method for low temperature coal tar fractions for production of middle distillates are indicated.

The processing of coal and coal products with hydrogen has been known for nearly a hundred years. A comparison of the ultimate analysis of different forms of fuel shows that addition of hydrogen is necessary to transform coal and coal tar to other forms of fuel. Berthelot was the first to note this fact and in 1870 he tried to convert coal and other solid fuels to liquid fuel using nascent hydrogen under pressure[1]. Using hydrogen iodide as source of hydrogen, he found that bituminous coal could be converted up to 60 per cent into a distillable oil; and that wood and charcoal could also be easily converted to paraffin hydrocarbons. On the other hand, charcoal prepared at a higher temperature, coke and graphite were not at all attacked by hydrogen. Dafert and Niklausz[2], Fischer and Tropsch[3] continued these experiments. The latter employed other sources of nascent hydrogen such as sodium formate, carbon monoxide along with steam, sodium carbonate and hydrogen in addition to hydrogen iodide and found that the younger the coal, the easier the hydrogenation. They also reported that with low temperature tar oils from bituminous coals, the hydrocarbon portion and the phenols boiling below 250°C. were unaffected while the phenols boiling between 250 and 340°C. were converted to alicyclic alcohols. However, use of nascent hydrogen for commercial purposes was out of the question.

In 1910, Bergius[4] started experiments with petroleum and coal tar products and using molecular hydrogen he achieved conversion of higher boiling products to lower boiling products without coke formation. Three years later, he extended this method to coal and achieved a conversion of coal up to 80 per cent into gaseous, liquid and other benzole-soluble products working at 400-450°C. and 150 atm. hydrogen pressure. At lower pressures (50 atm.) coke formation was predominant. Coals with more than 85 per cent carbon were found to be difficult to hydrogenate and the residue after hydrogenation was richer in carbon. To avoid coke formation due to local heating, coal ground to <1 mm. was mixed with a heavy oil (usually from the process itself) and the coal-oil paste was fed to the reactor. Based on these experiments, the first continuous plant of 30 tons/day capacity was put into operation in Mannheim in 1919 and various products such as petroleum residues, coal, etc. were tested. It was thus Bergius who showed for the first time that coal, coal tar and petroleum residues could be converted to lower boiling compounds with molecular hydrogen under pressure.

In 1924 Badische Anilin and Soda Fabrik (BASF) took up the hydrogenation of coal and coal tar and their experience in high pressure field, particularly ammonia and methanol synthesis proved of great help. The catalysts used for ammonia synthesis were found to lose their activity soon due to sulphur present in coal and coal tar. A systematic investigation with the different elements of periodic table led to the finding of molybdenum and tungsten compounds as being sulphur-resistant. In addition, these catalysts were able to alter the hydrogenation process so that the yield of desired product, especially gasoline increased and gas formation reduced. The use of carriers such as alumina over which catalyst was deposited was another important stage in the development of high pressure hydrogenation. By 1938 a number of high pressure hydrogenation plants were set up to process coal, coal tar and petroleum residues with installed capacity of 4 million annual tons[5].

After the war, high pressure hydrogenation of coal and tar for liquid fuel production lost its importance. The plants in West Germany have been switched over to processing petroleum crudes[6]. The plants in East Germany appear to have been in operation till recently. East Germany has large reserves of low grade coals and does not possess sufficient petroleum resources and so an appreciable portion of the liquid fuel requirements is met by hydrogenation of brown coal tar products[7]. In U.K. also which has no petroleum resources, work was carried out in the thirties at the Fuel Research Station and a commercial hydrogenation plant was set up at Billingham by Imperial Chemical Industries to process coal tar products[8]. This plant was in operation till 1958 when it was shut down. In U.S.A., high pressure hydrogenation was investigated at the Bureau of Mines, but no commercial plant appears to have been in operation.

Fig. 1 shows the ultimate analysis of coal, coal tar and petroleum products[9]. It is seen that the finished product is richer in hydrogen than the feed material and the difference in hydrogen content is maximum with coal and minimum with petroleum. Shale oil and coal tar lie intermediate. The conversion of coal to liquid fuel is, therefore, most difficult. Further, the starting material contains certain 'impurities' in the form of oxygen-, sulphur-, and nitrogen-containing compounds and these have to be removed during the process of the conversion to liquid fuels. These 'impurities' are maximum with coal, which again shows that coal is the most difficult to hydrogenate. In addition, coal contains ash and moisture which have to be removed before or during hydrogenation.

The raw materials and the finished liquid fuels differ not only in elementary composition but also in their molecular weights (Table 1)[10]. The molecular weight is reduced, which is brought about by a process of split-

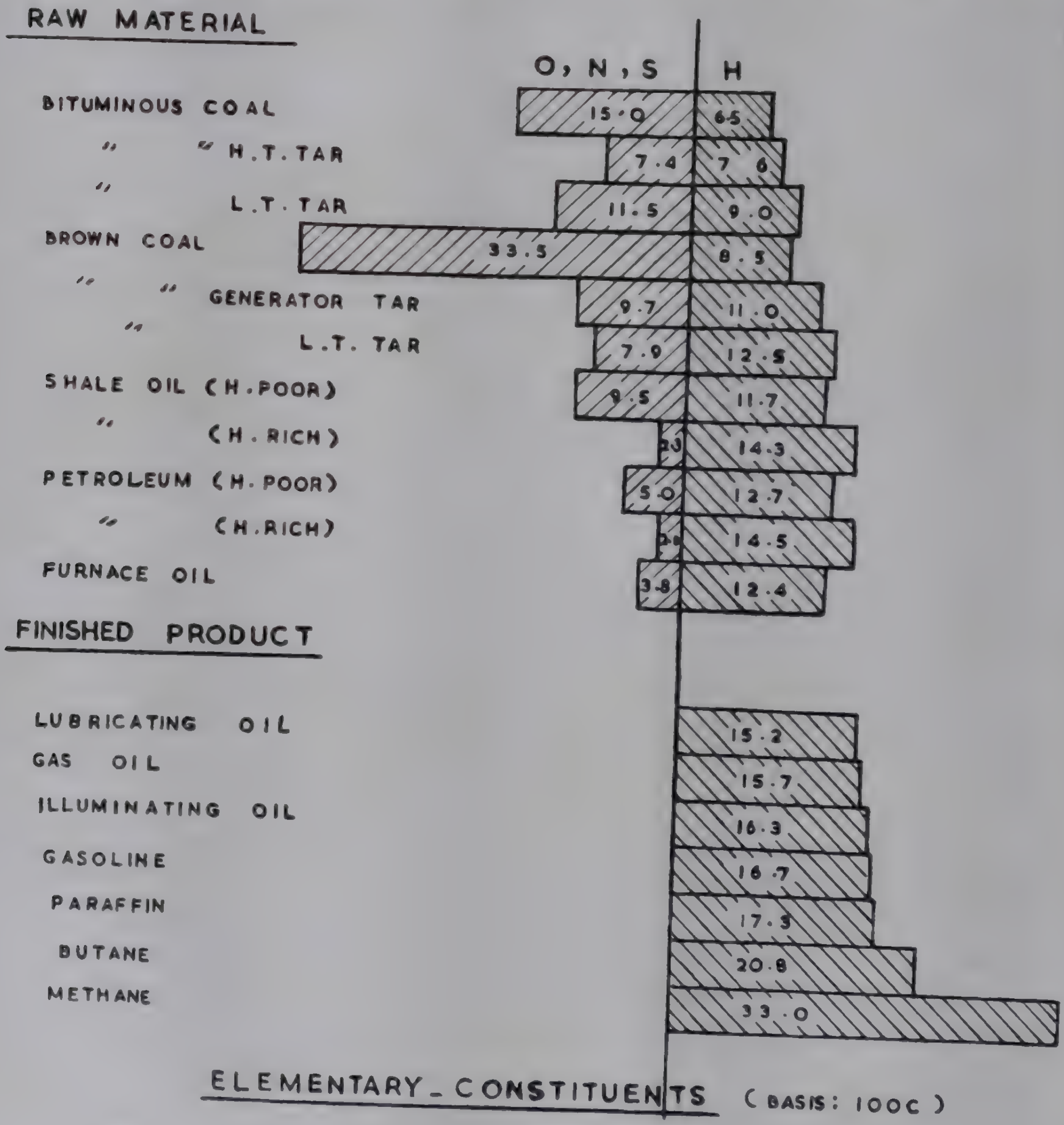


Fig. 1—Ultimate analysis of coal, tar and petroleum products

TABLE 1—MOLECULAR WEIGHTS OF RAW MATERIAL AND FINISHED PRODUCT

RAW MATERIAL	MOL. WT.		FINISHED PRODUCT	MOL. WT	
Bituminous coal		>5000	Lubricating oil	Approx.	400
High temperature tar from bituminous coal	Approx.	400	Gas oil	do	200
			Illuminating oil	do	150
L. t. tar from bituminous coal	Approx.	350	Gasoline	do	100
Brown coal		>5000	Paraffin	do	250
Generator tar from brown coal	Approx.	350	Butane	..	58
L. t. tar from brown coal	do	250	Methane	..	16
Shale oil	do	320			
Petroleum	do	400			

ting. This splitting has to be maximum with coal. The process of conversion of coal and coal products to liquid fuels therefore involves: (*i*) addition of hydrogen, (*ii*) removal of impurities, and (*iii*) reduction in molecular weight.

Thus coal is the most difficult to hydrogenate, next comes coal tar and then shale oil followed by petroleum. Even among coal tars, low temperature (l.t.) tars are easier to process than high temperature (h.t.) tars. With increasing temperature of carbonization, the proportion of high molecular compounds increases as manifested by diminished H/C ratio. These high boiling materials are refractory to hydrogenation and become adsorbed on catalyst. They also contain high proportion of free carbon which may be deposited on the catalyst bed, acting as filter [11].

H/C gives an index of the amenability of tar to hydrogen treatment. The higher this ratio the greater is the ease with which tar is treated and the smaller the amount of hydrogen required. The ratios of a few raw materials and finished products are given in Table 2 [12].

The value used for hydrogen in this ratio is that of the disposable hydrogen, i.e. hydrogen necessary to convert oxygen, sulphur and nitrogen to water, hydrogen sulphide and ammonia respectively. It can be seen from Table 2 that l.t. tar is more easily hydrogenated than h.t. tars. It has also been reported by King that l.t. tar fraction is more easily treated with hydrogen than the whole tar itself[12].

Hydrogenation can be done in two phases—liquid and vapour. In liquid phase, coal, high boiling coal tar or petroleum-residues are treated with hydrogen in presence of a finely divided catalyst. The product from

TABLE 2—H/C RATIOS OF VARIOUS MATERIALS

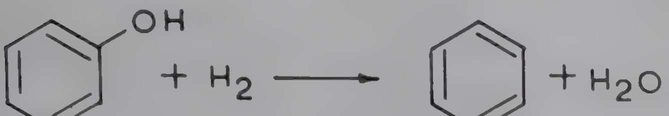
Material	Bituminous coal	H.T. tar (horizontal retort)	Vertical retort tar	L.T. tar	Pitch from H.T. tar	Pitch from L.T. tar	H.T. creosote	L.T. tar oil
% Carbon	84	91	85	82	92	81	87	82
Disposable hydrogen	4·1	5	6·1	6·9	4·1	5·6	6·0	7·9
H/C, atomic ratio	0·59	0·66	0·86	1·01	0·54	0·83	0·83	1·17

liquid phase hydrogenation and any raw material boiling below 325°C. can be treated in vapour or gas phase using the catalyst in lump form. When maximum conversion to petrol is desired, the gas phase hydrogenation itself is conducted in two stages. In the first step, the oxygen, nitrogen and sulphur compounds are removed using a catalyst containing molybdenum, tungsten or nickel compounds and the product obtained is then cracked in the second stage to lower boiling compounds using a catalyst containing aluminium silicate. In the case of liquid phase hydrogenation cheaper catalysts are used and the costly process of catalyst recovery is not usually practised. For brown coal, iron compounds on bauxite sludge and for bituminous coal tin compounds have been found suitable. For petroleum and coal tar residues, iron compounds on activated semicoke have been used[13].

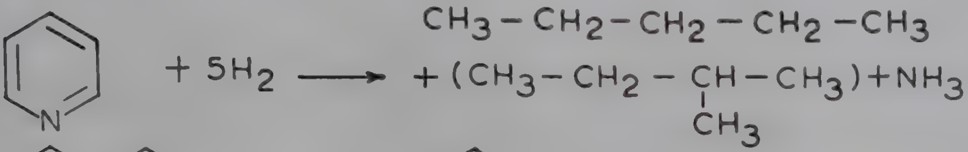
Hydrogenation process may be broadly classified as destructive and non-destructive. In destructive hydrogenation (hydro-cracking or hydrogenolysis) carbon—carbon bonds are broken and the fragments are saturated with hydrogen to produce lower boiling products. Here reduction in molecular weight is the main objective. The removal of oxygen-, sulphur-, and nitrogen-compounds is incidental only. Severe processing conditions are employed. High hydrogen pressures are required to minimize polymerizations and condensations leading to coke formation. For example, in the processing of coal a pressure of 300 atm. is used with brown coal and 700 atm. with bituminous coal. For coal tar residues a pressure of 200-300 atm. is used. The hydro-cracking of petroleum to increase the production of gasoline belongs to this category. Such high pressure plants are costly to build and operate.

Non-destructive hydrogenation or "hydro-treating" is employed to improve quality of feed without appreciably altering its boiling range. Here the removal of "impurities" is the main objective and milder conditions are used so that more unstable bonds between carbon and sulphur, oxygen and nitrogen are attacked. Olefins are saturated and unstable coke forms are converted to more stable materials. The pressures employed are of the order of 50-70 atm.

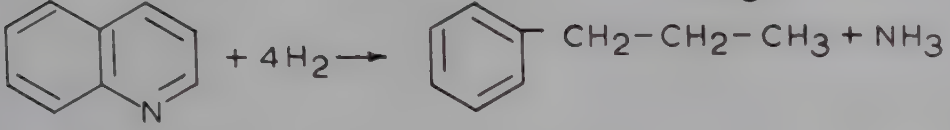
A few of the typical reactions taking place are shown by the following equations:



1

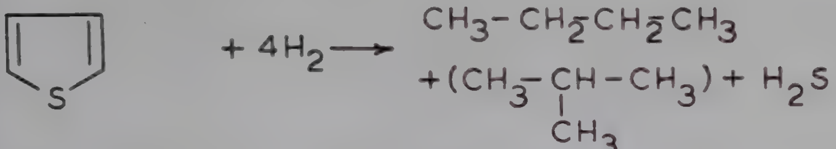

N
+ 5H2
CH3 − CH2 − CH2 − CH2 − CH3
+ (CH3 − CH2 − CH − CH3) + NH3
CH3

2


N
+ 4H2
CH2 − CH2 − CH3 + NH3

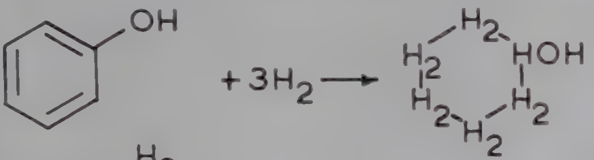
3

$R{-}SH + H_2 \longrightarrow R{-}H + H_2S$ 4

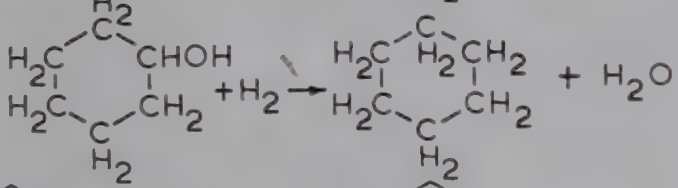

S
+ 4H2
CH3 − CH2 − CH2 − CH3
+ (CH3 − CH − CH3) + H2S
CH3

5

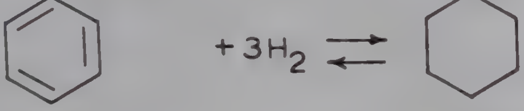
$CH_2{=}CH{-}R + H_2 \longrightarrow CH_3{-}CH_2{-}R$ 6


OH
+ 3H2
H2
H2
HOH
H2
H2
H2

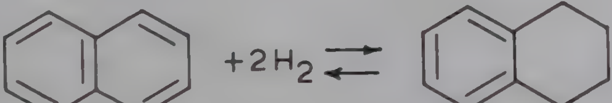
(7a)


H2
C
H2C
CHOH
H2C
CH2
C
H2
+ H2
C
H2C
H2
CH2
H2C
CH2
C
H2
+ H2O

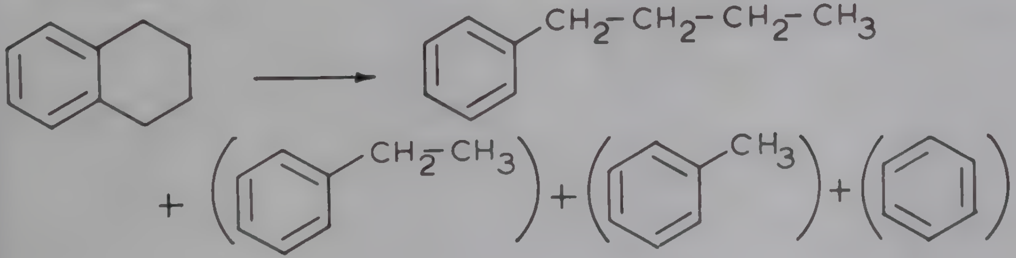
(7b)



8



9


CH2 − CH2 − CH2 − CH3
+
CH2 − CH3
+
CH3
+

10

The hydrogenation reactions 8 and 9 are reversible, hydrogenation occurring at lower temperatures and dehydrogenation at higher temperatures. The hydrogen requirements for most of these reactions range from 22 to 80 Nm^3/kg. mol.[14] The effect of pressure in these reactions is to favour the hydrogenation reactions. The rate of deterioration of catalyst is also reduced at higher pressures. This type of non-destructive hydrogenation is very common in the petroleum industry. With the availability of large quantities of hydrogen from catalytic reforming operations, various processes for hydro-treating have been developed such as unifining, autofining, etc. to process products ranging from gasoline to even lubricating oils. These processes reduce the sulphur content, remove the "impurities" and improve the stability of petroleum fractions. Hydro-treating the feed stock prior to catalytic cracking is claimed to improve its cracking properties as indicated by Table 4[15].

Results of hydro-treating of two distillates, one from bitumen sand and the other from shale oil are given in Table 3[16].

The refining of the feed stock subjected to platforming is essential as otherwise the platinum catalyst will be poisoned by the "impurities". This is achieved by hydro-treating the feed[17]. Now-a-days the refining of coke-oven benzole is done more efficiently with hydrogen and this method

TABLE 3—HYDRO-TREATING OF DISTILLATES FROM BITUMEN SAND AND SHALE OIL

	DISTILLATE FROM BITUMEN SAND		DISTILLATE FROM SHALE OIL	
	Feed	Product	Feed	Product
Density at 15·6°C.	0·959	0·897	0·859	0·802
Distillation data				
10 vol. % at °C.	198	166	169	137
50 do	414	361	270	232
80 do	515	422	..	..
90 do	..	..	335	317
Residue, vol. %	17·5	2·5	..	..
S, %	4·06	2·5	..	..
Bromine No.	50	10	..	..
N, %	..	..	1·44	0·004
Conradson test	6·8	1·02	..	..
Yield, vol. %	..	101	..	102
Hydrogen consumed, cu.m./ton	about 150		about 220	

TABLE 4—HYDRO-TREATING CATALYTIC CRACKING FEEDS

	WIDE RANGE VIRGIN FROM HIGH SULPHUR CRUDE		FROM VISBREAKING OF WEST TEXAS RESIDUE		WIDE RANGE VIRGIN FROM WEST TEXAS SWEET CRUDES	
	Charge	Product	Charge	Product	Charge	Product
Pressure, psi	..	500	..	500	..	500
Temp., °F.	..	760	..	750	..	750
Hydrogen flow rate cu. ft/bbl oil	..	5000	..	2000	..	2000
LHSV	..	1·0	..	1·0	..	1·0
Liquid recovery, %	..	101·9	..	100·0	..	100·5
Gasoline produced, vol. % of feed	..	5·5	..	0·0	..	0·0
Hydrogen consumed cu. ft/bbl	..	300	..	220	..	110
% Desulfurization	..	92	..	78	..	88
Cracking feed inspection API gravity	24·8	30·2	24·6	27·2	29·8	31·9
Vacuum distillation corrected to 760 mm. Hg						
I.B.P. at °F.	440	438	506	469	493	453
10 vol., % at °F.	517	493	650	621	585	558
50 do	741	682	940	911	957	939
90 do	1006	938	1099	1098	957	939
S, %	2·66	0·24	0·72	0·16	0·51	0·06
N, %	0·09	0·04	0·16	0·16	0·08	0·04
Carbon residue Ramsbottom, wt %	0·81	0·13	1·50	0·67	0·32	0·08
Heavy metals, ppm NiO	0·55	<0·05	1·7	<0·05	0·18	..
V_2O_5	0·53	<0·05	1·9	<0·05	0·11	..

has almost completely displaced the earlier method of refining with sulphuric acid[18].

Similar treatment of coal tar distillates under mild conditions with hydrogen has also been reported by Birthler[19]. The results obtained during the refining of brown coal tar distillate at 50 atm. is given in Table 5.

TABLE 5—HYDROFINING OF BROWN COAL TAR DISTILLATE

	FEED		PRODUCT	
	(1)	(2)	(1)	(2)
Sp. gr. at 20°C.	0·866	0·925	0·824	0·860
Up to 200°C., vol. %	22	2	34	12
S, %	0·80	1·1	0·06	0·1
O+N, %	2·76	4·23	0·25	0·28
Creosote, vol. %	8·8	16·6	0·1	0·8
Cetane No.	36 (nom.)	30 (mot.)	46 (nom.)	42 (mot.)
Yield, %			over 85	

The hydro-treating can be carried out in gas phase as well as in liquid phase. The TTH and MTH processes developed in Germany during the war were intended to treat brown coal tars and operate at rather high pressure of 300 atm.[20] These processes operate in liquid phase with fixed bed catalyst. By gas phase hydro-refining shale oil was converted to diesel oil. Production of jet fuels and water-white burning oil were possible by hydro-refining. Recent investigations by BASF have shown that l.t. tars could be hydrogenated to gasoline and diesel fuel by liquid and gas phase hydrogenated at a pressure of 250 atm. A product lying in the diesel fuel range with a cetane number of about 47 is reported to have been obtained[21]. The patented Varga process treats brown coal tar in liquid and gas phase in single stage at a hydrogen partial pressure of 70 atm.[22] Work on hydrogenation of l.t. tar oils to diesel oils has recently been reported from Central Fuel Research Institute, Jealgora[23].

This type of non-destructive hydrogenation of coal tars is of particular significance to India. The imbalance between production and demand of diesel oils has reached serious proportions. While gasoline is available for export, large quantities of diesel fuel and middle distillates are being imported. The requirements of these fractions are bound to go up with the increasing dieselization of railways and increased standards of living of people. With the setting up of a number of low temperature carbonization plants in the country, large quantities of l.t. tar will be available for processing. By converting the middle distillates by hydro-treating l.t. tar fractions, at least a portion of the country's requirements for middle distillates can be met.

One more aspect, apart from production of middle distillates—from l.t. tar, deserves special mention. Coal tar has always been an important source of raw material for the production of chemicals. L.t. tar contains a large proportion of high boiling tar acids which can be easily dealkylated to phenol and cresols which will find ready market. This aspect is being investigated in Germany[24] and other countries[25]. The demand for benzene, toluene and xylene was till recently met by coal carbonization products but the demand is increasing so rapidly that alternate sources from petroleum are being explored. Hydrofining of l.t. tar fractions yields some of these aromatic hydrocarbons also.

Thus l.t. tar can be utilized not only for the production of middle distillates and other liquid fuels but also for the production of valuable chemicals.

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Catalyst for Medium Pressure Hydrogenation of Low Temperature Tar Oils: Part I

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Conditions for the preparation of molybdena-cobalt oxide-silica-alumina catalysts of varying compositions were studied using impregnation technique.

Surface area of the alumina carrier increases on deposition of molybdena and is maximum for MoO_3 content of 12-16 per cent, when MoO_3 forms a monomolecular layer on the surface of the carrier. Further increase in the MoO_3 content results in decrease in surface area and diminution in its activity.

The incorporation of about 8 per cent silica in the molybdena-cobalt oxide-alumina catalyst improves its activity for hydrogenation of phenol to benzene and an increase in the cobalt oxide content enhances considerably its capacity for converting benzene into cyclohexane, suggesting that the catalyst having approximately the composition: MoO_3—9, CoO—5, SiO_2—7, and Al_2O_3—79 per cent will give the desired conversion of olefines, tar acids and tar bases in the low temperature tar oils, to the corresponding hydrocarbons.

The suitability of molybdena-alumina catalyst for hydrogenation of tar is known[1]. However, information on preparation of the catalyst is mostly covered by patents. Slight changes in the process affect its properties and therefore, in order to prepare a catalyst with reproducible characteristics and behaviour, it is essential that each step in its preparation be properly controlled. Work has been undertaken on the preparation of a suitable MoO_3. CoO . SiO_2. Al_2O_3 catalyst, and its standardization and the study of its hydrogenation properties.

MATERIALS AND METHODS

Alumina Carrier. Aluminium hydroxide precipitated from chemically pure $AlCl_3$. $6H_2O$ and $AlCl_3$ anhydrous and C. P. grade sample of $Al(OH)_3$ (B.D.H.) were used for the preparation of alumina carrier. Aluminium hydroxide was precipitated at *p*H of 7·5-8·0 by adding ammonia solution (0·936 sp. gr.) to 6 per cent aluminium chloride solution. Beyond a *p*H of 8, aluminium hydroxide dissolved, decreasing the yield of alumina. The precipitate was allowed to settle overnight, washed with dilute ammonia and finally with distilled water and dried at 150°C. Aluminium hydroxide was heated to 550°C. at a rate of 3°C. per minute and maintained at that temperature for 3 hr to get activated alumina.

Silica-alumina Carrier. Silica gel was prepared by reacting 20 per cent sodium silicate (Na_2O. 3·3 SiO_2) solution with hydrochloric acid (1·1 sp. gr.). It was mixed with requisite amount of precipitated aluminium hydroxide, dried at 150°C. and heat activated at 550°C.

The alumina and silica-alumina carriers were powdered to pass through 200 mesh B.S.S. and active components were incorporated in the carriers by the usual impregnation method.

Deposition of Molybdena. Aqueous solutions of ammonium molybdate $(NH_4)_6$. Mo_7O_{24}. $4H_2O$ of varying concentrations were added to the previously evacuated alumina carrier. The solution was decanted and filtered. The impregnated carrier was dried at 150°C. and heated at 500°C., when the molybdate is decomposed to MoO_3.

Addition of Promoter. Cobalt oxide promoter was similarly deposited on the catalyst by bringing the catalyst into contact with an aqueous solution of cobalt acetate $Co(C_2H_3O_2)_2.4H_2O$ followed by drying at 150°C and igniting at 500°C. at which temperature the acetate is converted into oxide.

Evaluation of the Catalyst. Chemical analysis of the catalyst was done by standard methods[2,3]. Surface area was determined by benzene adsorption method at 750°C. as it is quick and gives reproducible results. Determination of heat of wetting for methanol and phenol was also done. The catalysts, after reduction with hydrogen at 450°C. for 3 hr, were evaluated for hydrogenation of phenol to benzene, benzene to cyclohexane and tetralin to decalin, using "Parr" high pressure rocking type autoclave. Hydrogenation was carried out at 1500-4500 psi and temperature of 350°C. for 3 hr using 5 per cent by weight of the freshly reduced catalyst. The extent of conversion of phenol to benzene was determined by estimating residual phenol by bromide-bromate method and that of the benzene to cyclohexane and tetralin to decalin by the change in refractive indices.

Performance Test. The catalyst containing 12·3 per cent MoO_3, 1 per cent CoO and 86·7 per cent Al_2O_3 was used for hydrogenation of a low temperature tar fraction with a boiling range of 225-290°C. and neutral oil

TABLE 1—PROPERTIES OF CATALYSTS AND CATALYST CARRIERS

CARRIER PREPARED FROM	CONCENTRATION OF AMMONIUM MOLYBDATE SOLUTION, %	MoO_3 DEPOSITED, %	SURFACE AREA, sq.m./g.	MoO_3 CARRIER (by weight)	HEAT OF WETTING FOR Methanol (cal./g.)	HEAT OF WETTING FOR Phenol (cal./g.)
$AlCl_3$	..	0	72	..	..	..
	5	16	86	..	..	..
Al $(OH)_3$	..	0	175	..	19·60	6·42
	5	8·7	354	..	39·33	12·72
	10	16·7	190	..	20·97	6·78
$AlCl_3.6H_2O$	..	0	93	..	..	..
	5	16·5	218	0·19	26·86	8·72
	10	33·1	104	0·38	..	..
	25	36·2	40	0·57	..	..
	..	8	220	..	25·04	8·10
	4	12·1	212	0·14	..	..

TABLE 2—HYDROGENATION OF PHENOL, BENZENE AND TETRALIN

CATALYST	MoO_3 (%)	CoO (%)	SiO_2 (%)	% CONVERSION Phenol to benzene (in presence of thiophene)	% CONVERSION Benzene to cyclohexane	% CONVERSION Tetralin to decalin
$MoO_3.Al_2O_3$	8	..	..	14	5	10
do	33·1	..	..	..	..	14
do	36·2	..	..	..	..	20
MoO_3. CoO. SO_2 Al_2O_3	12·5	1·0	..	37	7	25
do	16·54	0·9	..	40	10	34
MoO_3. CoO. SiO_2. Al_2O_3	9·31	1·78	7·98	55·4	10·0	..
do	8·93	2·83	6·90	45·9	22·0	..
do	8·89	3·78	6·48	42·0	36·0	..
do	9·00	4·48	6·68	40·0	46·0	..
do	10·06	4·87	6·78	39·0	50·0	..
do	12·05	1·0	..	37·0	..	..
do	10·15	1·2	2·07	40·7	..	..
do	9·31	1·7	7·88	55·4	..	..

thereof, in a continuous bench scale unit. After a preliminary reduction of the catalyst with hydrogen for 4 hr at 450°C., runs were conducted at a pressure of 70 kg /sq. cm., at a space velocity of about 0·66 V/V/hr, at a hydrogen/oil ratio of approximately 500 and at temperatures of 400°, 450° and 480°C. For comparison, experiments were also conducted with a commercial catalyst containing 12·5 per cent MoO_3, 0·67 per cent CoO, 5·8 per cent SiO_2 and 81·0 per cent Al_2O_3 under identical conditions.

RESULTS AND DISCUSSION

The properties of the different catalysts are given in Table 1. The results of hydrogenation are presented in Table 2 and the performance data are described in Tables 3 and 4.

Incorporation of Active Components. Amount of molybdenum oxide deposited on the carrier is approximately proportional to the concentration of ammonium molybdate solution (Fig. 1). Assuming that unimolecular

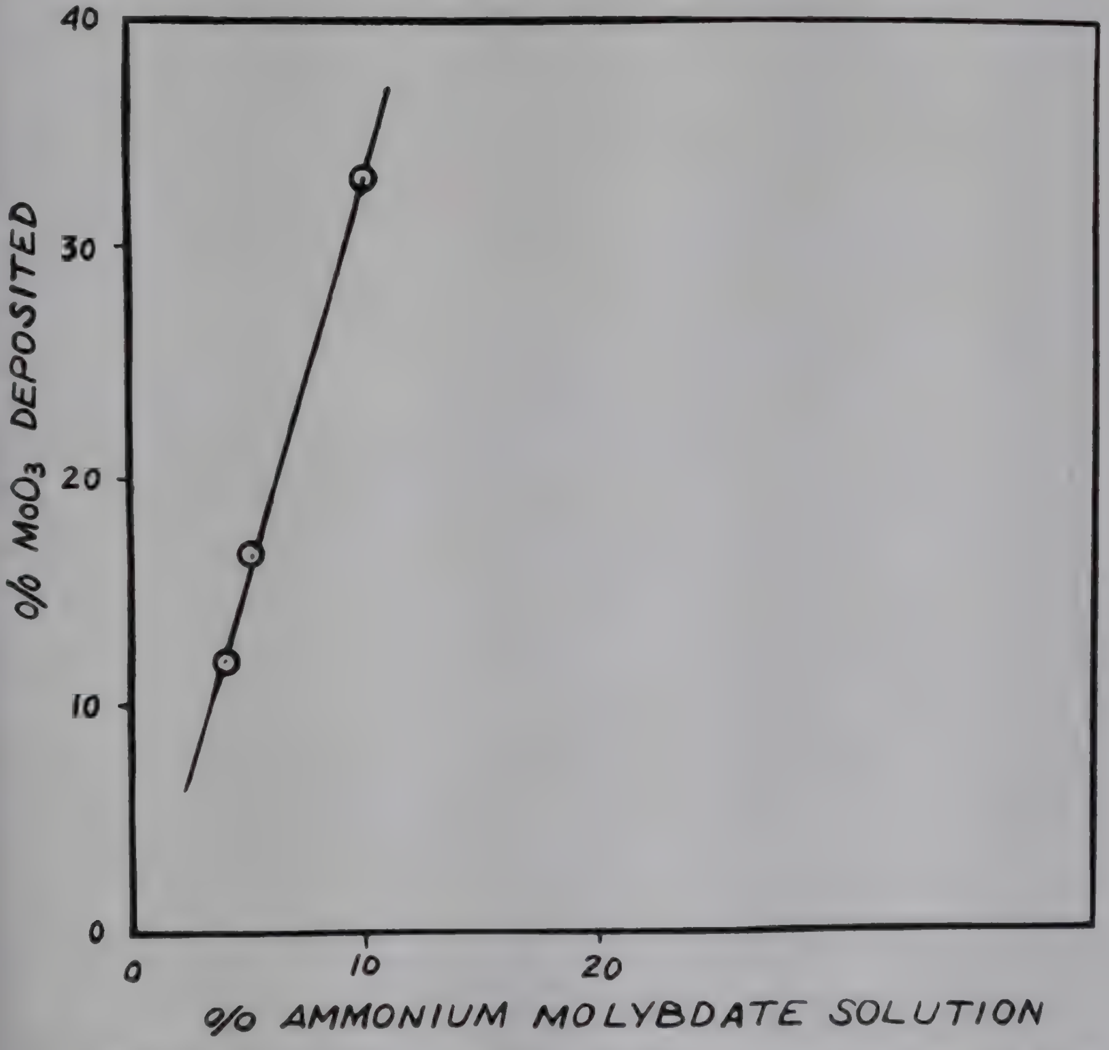

FIG. 1—MOLYBDENUM OXIDE DEPOSITED AT DIFFERENT CONCENTRATIONS OF AMMONIUM MOLYBDATE SOLUTION

TABLE 3—HYDROGENATION OF NEUTRAL OIL

TEMP. OF HYDROGENATION, °C. CATALYST	450 PREPARED IN THE LABORATORY	450 COMMERCIAL CATALYST SULFIDED	450 COMMERCIAL CATALYST FRESH	400 PREPARED IN THE LABORATORY	400 COMMERCIAL CATALYST FRESH	480 PREPARED IN THE LABORATORY	480 COMMERCIAL CATALYST SULFIDED
Sp. gr.	0·8577	0·8604	0·8552	0·8708	0·8638	0·8602	0·8491
n_d^{20}	1·4940	1·4930	1·4935	1·4965	1·4860	1·5013	1·4883
Sp. gr. of 0-200°C. fraction	0·7909	0·7858	0·7895	. .	. .	0·7797	0·7782
n_d^{20} of 0-200°C. fraction	1·4592	1·4530	1·4600	1·4548	1·4638	1·4572	1·4452
Sp. gr. of 200-340°C. fraction	0·8742	0·8721	0·8664	0·8779	0·8684	0·8901	0·8759
n_d^{20} of 200-340°C. fraction	1·5010	1·4965	1·4990	1·4998	1·4875	1·5148	1·4992
Distillation Data							
10% Vol. at, °C.	166	188	171	213·5	214	121	141
50% Vol. at, °C.	252	256	250	263·5	262	243	239·5
90% Vol. at, °C.	308	311	305	319	311·5	310	302·5
Aniline point, °C.	37·7	37·6	38·7	37·6	43·3	26·3	31·2

(Contd.)

TABLE 3—*Contd.*

Temp. of hydrogenation, °C.		450	450	450	400	400	480	480
Catalyst		Prepared in the laboratory	Commercial catalyst sulfided	Commercial catalyst fresh	Prepared in the laboratory	Commercial catalyst fresh	Prepared in the laboratory	Commercial catalyst sulfided
F.I.A. Analysis, vol. %								
Total product:	Aromatics	50·4	50·0	50	52·6	45·5	60	53·1
	Olefines	0·7	0·8	0·7	1·6	0·9	1	1·0
	Saturates	48·9	49·2	49·3	46·4	53·6	39	45·9
0-200°C. fraction:	Aromatics	47·2	36·0	40·2	41·5	32·4	. .	36·3
	Olefines	1·0	0·6	0·5	0·8	1·1	. .	0·8
	Saturates	51·8	63·4	59·3	57·7	66·5	. .	62·9
200-340°C. fraction:	Aromatics	51·8	52·4	50·3	51·9	51·9	. .	57·9
	Olefines	1·2	1·5	0·5	0·7	0·7	. .	0·8
	Saturates	47·0	46·1	49·2	47·4	47·4	. .	41·3
Fraction up to 200°C., vol. %		17·5	13·0	15	7	6·5	26·5	25
Furfural insoluble, vol. %		52·6	46·5	47·5	56·5	62·5	39	42
n_d^{20} of furfural insoluble		1·4635	1·4612	1·4650	1·4688	1·4650	1·4667	1·4528

TABLE 4—HYDROGENATION OF TAR OIL

Temp. of hydrogenation, °C.	Raw material	400	450	480
Sp. gr.	0·9552	0·9062	0·8745	0·8624
n_d^{20}	..	1·5160	0·5025	1·5022
Sp. gr. of 0=200°C. fraction	..	0·8387	0·8034	0·8049
n_d^{20} of 0=200°C. fraction	..	1·4775	1·4630	1·4662
Sp. gr. of 200=300°C. fraction	..	0·9124	0·8931	0·8949
n_d^{20} of 200=300°C. fraction	..	1·5178	1·5125	1·5170
Tar acids	24 (vol. %)	10·1 (wt %)	traces	traces
Tar bases, wt %	5·67	2·58	0·75	1·27
Neutral oil: Aromatics, vol. %	56·1	70·7	61·7	61·4
Olefins, ,,	17·6	1·5	0·9	1·1
Saturates, ,,	26·3	27·8	37·4	37·5
Aniline point, °C.	..	25·7	26·8	24
Distillation, 10 % vol.	235	191	147	124
50 % vol.	266·5	253	254	235
90 % vol.	326·5	317	311·5	309
Fraction up to 200°C, vol. %	..	13·2	23	35

layer of molybdenum oxide is formed on alumina, the ratio of MoO_3: Al_2O_3 in the catalyst works out to be 0·17 : 1. These ratios calculated for catalysts prepared using different concentrations of ammonium molybdate solutions are given in Table 1. For the catalyst prepared using 4 per cent and 5 per cent aqueous ammonium molybdate, MoO_3: Al_2O_3 ratios are 0·14 : 1 and 0·19 : 1 and the molybdena contents are 16 per cent and 12·1 per cent respectively. Thus the catalyst containing desired MoO_3 content may be prepared by taking suitable concentration of ammonium molybdate solution for impregnation. In practice catalyst containing 12 per cent MoO_3 is preferred and is obtained by adding 10 cc. of 4 per cent ammonium molybdate solution per gram of alumina carrier.

Similarly, desired amounts of cobalt oxide can be incorporated in the molybdena-alumina catalyst by using cobalt acetate solution of requisite concentration. CoO content in the catalyst bears a linear relationship with the cobalt acetate solution used for impregnation (Fig. 2). For depositing 1 per cent cobalt oxide, 8 cc. of 0·5 per cent cobalt acetate solution per gram

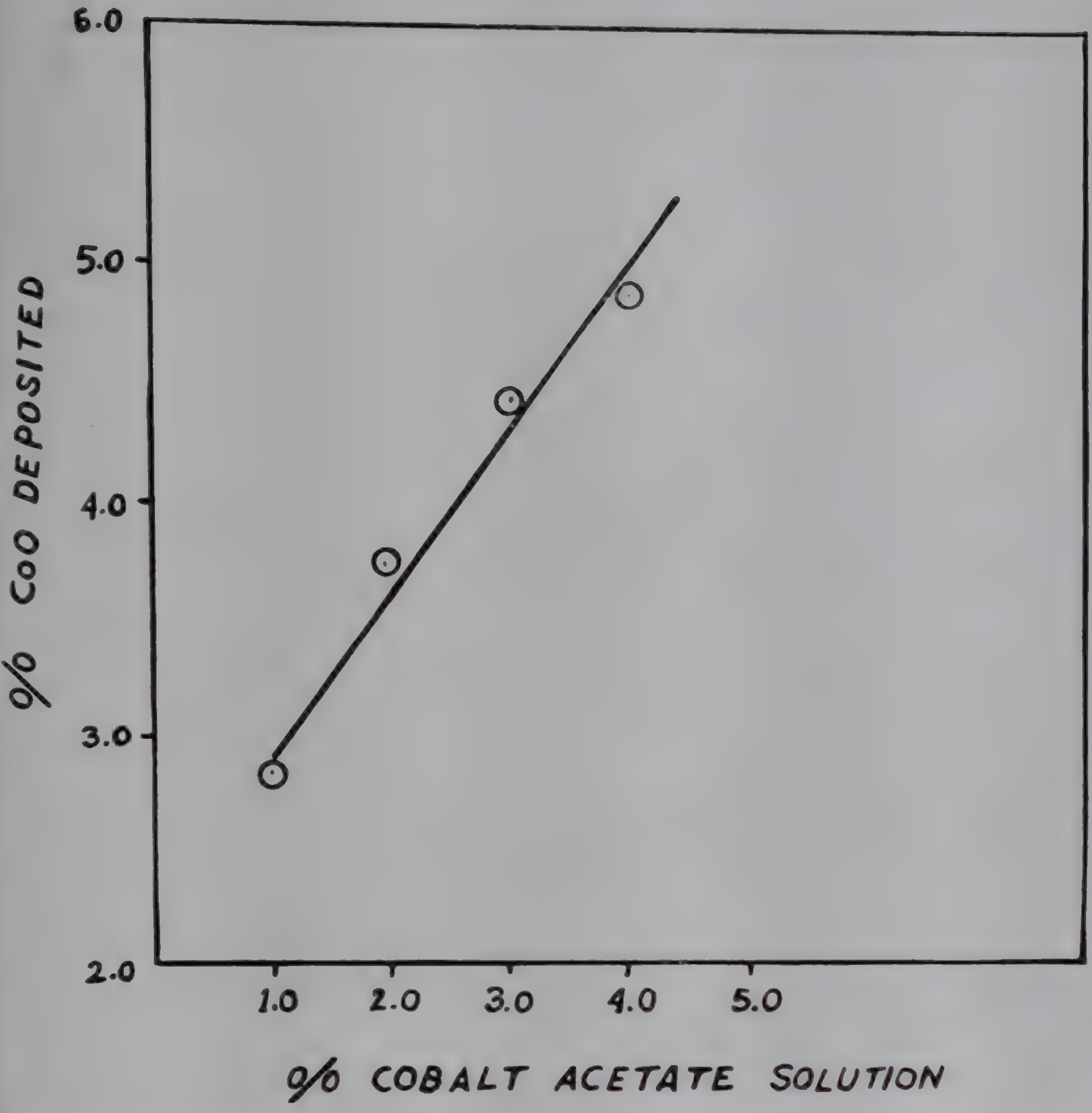

FIG. 2—COBALT OXIDE DEPOSITED AT DIFFERENT CONCENTRATIONS OF COBALT ACETATE SOLUTION

of the catalyst is required. The incorporation of cobalt oxide prior to deposition of molybdena on the alumina carrier gave an inferior catalyst as compared to the catalyst prepared as above.

Surface Area. Surface area increases on the deposition of molybdena on alumina from about 75 to 200 sq. m./g. in case of precipitated alumina and from 175 to 354 sq.m./g. for B.D.H. alumina. The catalyst with MoO_3 content greater than that required for forming monomolecular layer showed a decrease in surface area (Fig. 3). There is slight variation in surface area of catalyst by depositing about 1 per cent of cobalt oxide promoter.

The heat of wetting values plotted against the surface area show linear relationship (Fig. 4). The heat of wetting for methanol is nearly thrice that for phenol. Factors for computing surface area (sq.m./g.) of the catalyst from heat of wetting for methanol and phenol (cal./g.) are 9 and 27 respectively.

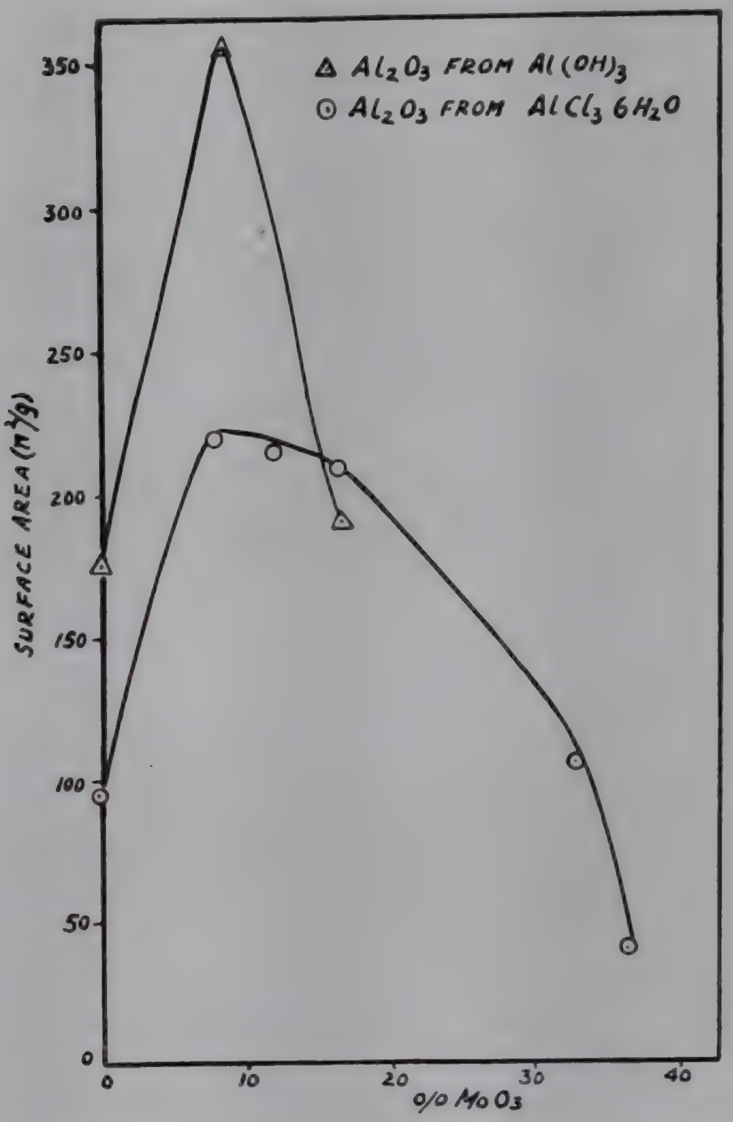

FIG. 3—SURFACE AREA OF CATALYST WITH DIFFERENT MOLYBDENUM OXIDE CONTENTS

Hydrogenation. It is observed that for the same molybdena content, catalyst supported on alumina prepared from $AlCl_3 . 6H_2O$ exhibited higher activity for hydrogenation of phenol to benzene and of tetralin to decalin than catalysts supported on alumina carriers obtained from anhydrous aluminium chloride and aluminium hydroxide. The deposition of more than 12·5 per cent of MoO_3 on alumina was found not to improve the activity of the catalyst. It was further seen that the incorporation of about 8 per cent silica in the above catalyst enhanced its activity for hydrogenation. The increase in the conversion of phenol to benzene approximately corresponded to the increase in the silica content of the catalyst (Fig. 5).

Freshly reduced catalyst invariably exhibited improved activity. The reduced catalyst deteriorated in its activity on storage. On reduction, MoO_3 changes to MoO_2 which is the actual catalyst responsible for acceleration of the reaction. Since the catalyst is to be used for hydrogenation of tar fractions which contain up to 0·5 per cent of sulphur, the experiments on

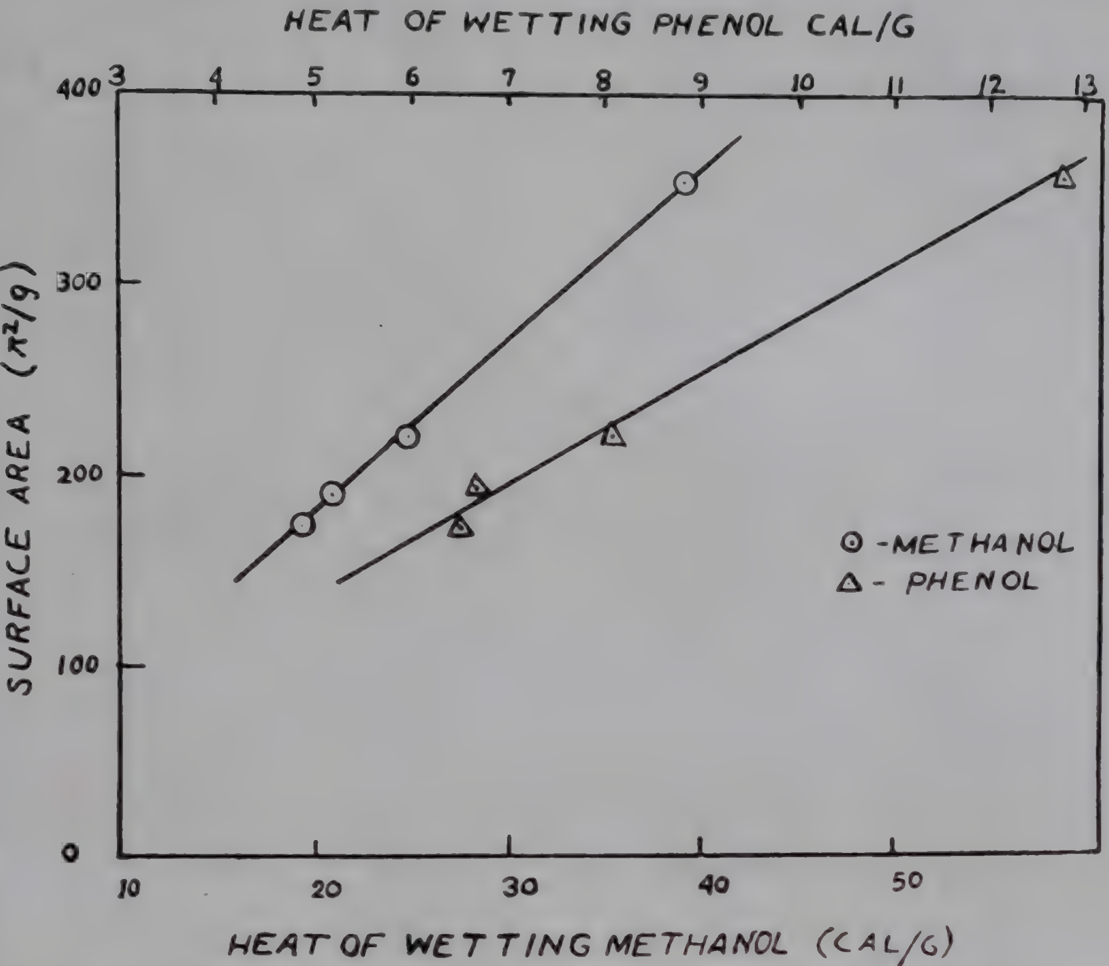

Fig. 4—Relationship between heat of wetting and surface area

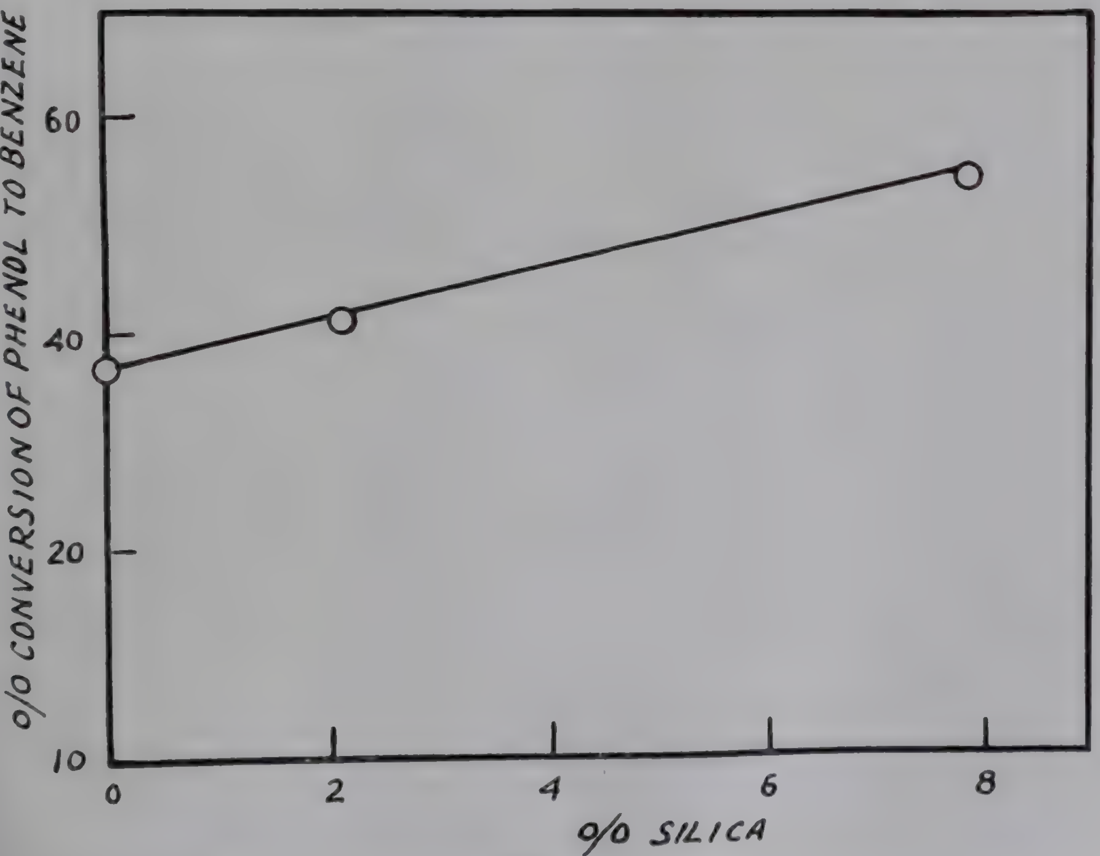

Fig. 5—Conversion of phenol at various silica contents

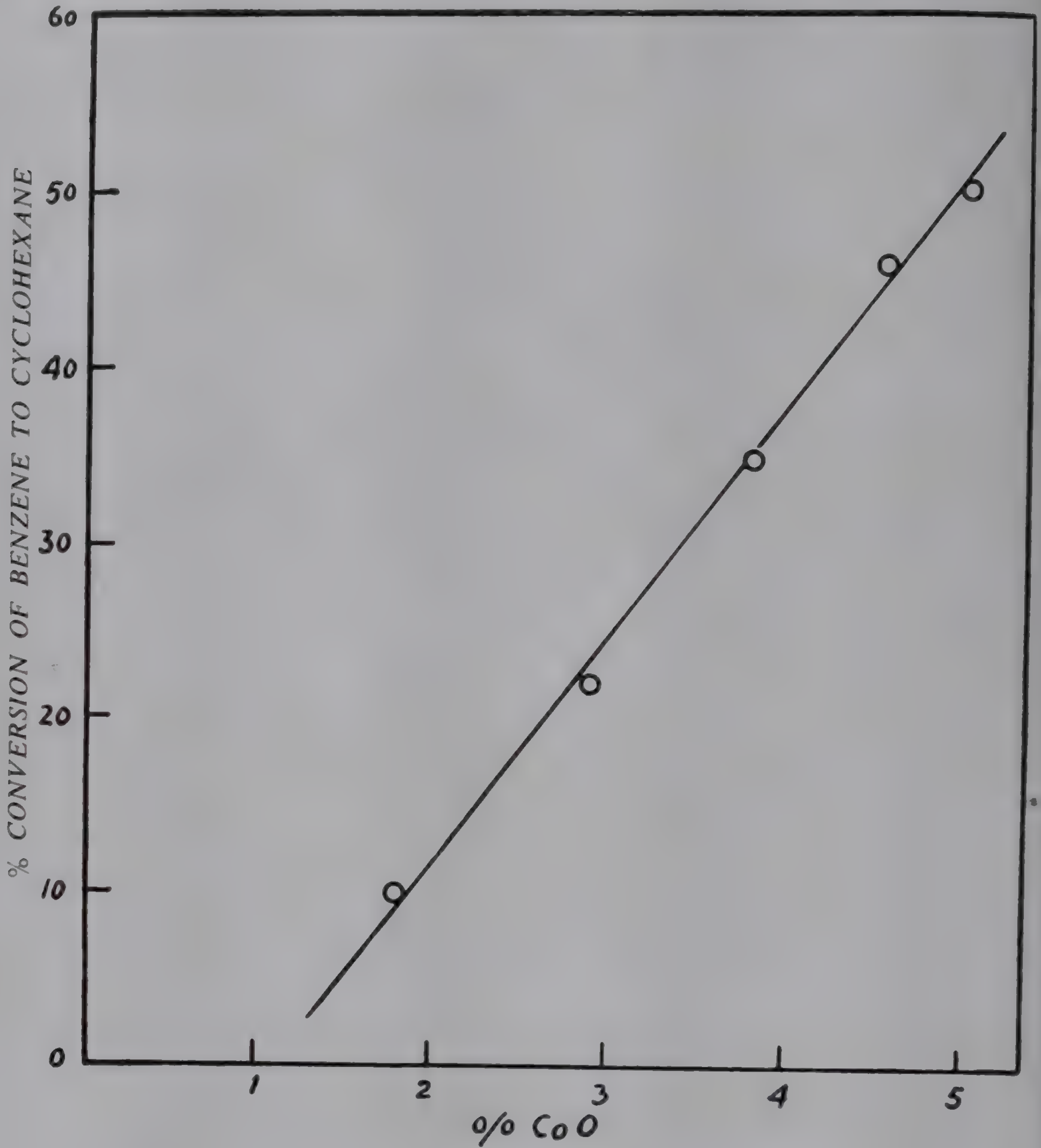

FIG. 6—CONVERSION OF BENZENE AT VARIOUS COBALT OXIDE CONTENTS

hydrogenation were carried out in the presence of 0·5 per cent thiophene. It was observed that the presence of sulphur greatly accelerated the hydrogenation reaction as molybdenum oxide under these conditions changes to molybdenum sulphide which is more active as it is readily reduced to MoS_2.

Distillation data of the product from hydrogenation of neutral oil and tar oil are given in Tables 3 and 4. It will be seen that in the case of neutral oil, aniline point of the product decreases as the temperature of hydrogenation is increased beyond 450°C. In the case of tar oil fraction (225-290°C.) at 450°C. all the tar acids are completely removed but the aniline point is low as compared to that of the hydrogenated product from neutral oil and the product still contains 0·75 weight per cent of tar bases.

As the content of saturated hydrocarbons produced was low, it was considered desirable to modify the catalyst by increasing the proportion of cobalt oxide. Catalysts were prepared using silica-alumina carrier keeping molybdena content constant (9 per cent) and varying cobalt oxide from 1-5 per cent at the expense of alumina. They were evaluated for hydrogenation of phenol to benzene and benzene to cyclohexane at 350°C. and 1500 psi and 4500 psi respectively. It was observed that with these catalysts there was a slight decrease in the conversion of phenol to benzene but the conversion of benzene to cyclohexane increased from 10 to 50 per cent as the CoO content was increased from 1·78 to 4·87 per cent. The increase in the per cent conversion of benzene to cyclohexane bears approximately linear relationship with the cobalt oxide content of the catalyst (Fig. 6).

It is proposed to use the catalyst having composition MoO_3—9 per cent, CoO—5 per cent, SiO_2—7 per cent and Al_2O_3—79 per cent in a continuous pilot plant for hydrogenation of low temperature tar fractions. This catalyst is expected to hydrogenate the olefines, tar acids and tar bases to the corresponding hydrocarbons and to further saturate the aromatics to naphthenic hydrocarbons.

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Studies on Medium Pressure Hydrogenation of Low Temperature Coal Tar Fractions

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Experiments on medium pressure hydrogenation of low temperature coal tar fractions using a batch autoclave and a continuous bench-scale unit with a fixed bed of catalyst are reported. In both these investigations, a commercial desulfurization catalyst—Cobalt Molybdate on Alumina was used. The effect of catalyst concentration and duration of hydrogenation as well as rehydrogenation of once hydrogenated product were investigated in the batch autoclave. In the continuous unit, the infuence of temperature, pressure of hydrogenation and the space velocity were studied.

Hydro-refining of petroleum fractions is a common practice in the petroleum industry. This treatment carried out with hydrogen under mild conditions is intended to remove oxygen, nitrogen and sulphur-compounds from the feed and to saturate the olefinic double bonds without producing any appreciable reduction in the boiling range. Such treatment of petroleum fractions has been investigated by several workers. Similar treatment of coal tar fractions under mild conditions has not been much investigated.

Birthler[1,2] has carried out investigations on hydrogenation of brown coal tar fractions. Work on hydrogenation of low temperature (l.t.) tar fractions has also recently been reported from Central Fuel Research Institute, Jealgora[3]. The present paper briefly describes the investigations carried out at this Laboratory, both with a batch autoclave and with a bench-scale continuous unit using l.t. coal tar fractions. The tar was obtained from the 25 tons/day Lurgi-Spuelgas low temperature carbonization pilot plant processing non-caking coal from Kothagudem. The tar was subsequently distilled in a 3 ton/batch pot still. A commercial desulfurization catalyst consisting of cobalt oxide-molybdenum oxide deposited on aluminium oxide was used in these studies.

EXPERIMENTS IN BATCH AUTOCLAVE

A batch autoclave of 1 litre capacity supplied by Parr Instrument Co. and provided with a stirrer was used. A tar fraction (B. P. 250-350°C.) formed the feed material. The required quantity of powdered catalyst was mixed with a small quantity of the tar oil and taken in the stainless steel container to which more oil was added. The autoclave was assembled and pressurized at room temperature with hydrogen after flushing it twice or thrice so that the hot pressure at 350°C. was about 900 psi. The autoclave was heated to 350°C. and maintained at this temperature for different durations of time. The autoclave was cooled and pressure released. The catalyst was filtered off and used in a few experiments. The product was analysed according to standard methods.

Effect of Catalyst Concentration. In this series of experiments, hydrogenation was carried out at 900 psi (hot pressure) and 350°C. for 3 hr with catalyst concentrations of 3, 5, 10 and 20 per cent. The results are reported in Table 1. It is seen that when the catalyst concentration is increased from 3 to 20 per cent there is no appreciable change in the tar acid content or in the aromatic hydrocarbon content. The product still contains about 4 per cent of olefins, compared to 10 per cent in the feed oil.

Effect of Duration of Hydrogenation. In this series, the duration of hydrogenation was varied from 3 to 12 hr keeping the catalyst concentration at 10 per cent and the temperature and pressure of hydrogenation at 350°C. and 900 psi respectively. The results are presented in Table 2. When the period of hydrogenation is increased from 3 to 6 hr, the tar acids decrease from 11·2 to 5·6 vol. per cent. Further increase to 12 hr reduces the tar acid content to 3·8 per cent. However, the aromatic content is not decreased. The product contains 0·11 per cent of sulphur even after 12 hr of hydrogenation.

Properties of Catalyst. Cobalt molybdate catalyst is noted for its long life and activity. It retains its activity even in presence of sulphur compounds. This was tested in this series of experiments. The catalyst after each run was filtered and used to hydrogenate a fresh batch of tar oil. The results are presented in Table 3. It is seen that the catalyst even after being used four times was found to be active. The tar acid content of the product was 5·6 per cent with the catalyst which has been used four times as compared to 10·8 per cent with fresh catalyst.

Effect of Rehydrogenating the Product. In this series the once hydrogenated product was rehydrogenated with fresh catalyst under the same conditions. A portion was rehydrogenated with used catalyst also. The results are shown in Table 4. It is seen that rehydrogenation improves

TABLE 1—INFLUENCE OF CATALYST CONCENTRATION

(Pressure, 900 psi; Temp., 350°C.; Duration, 3 hr)

	CATALYST CONCENTRATION				
	Feed oil	3%	5%	10%	20%
Sp. gr.	0·961	0·938	0·937	0·931	0·932
Tar acid content, vol. %	20	13·6	12·4	11·2	10·8
up to 200°C., vol. %	..	5	6	12	5
up to 250°C., vol. %	10	22·5	23	32	23
up to 300°C., vol. %	70	68·5	70	78	73
Paraffins and naphthenes, vol. %	12·9	21·0	22·1	27·5	24·7
Olefins, vol. %	10·1	4·5	3·8	4·0	3·8
Aromatic hydrocarbons, vol. %	57·0	60·7	61·7	57·3	60·6

TABLE 2—EFFECT OF DURATION OF HYDROGENATION

(Pressure, 900 psi; Temp., 350°C.; Catalyst concentration, 10%)

	FEED OIL	HYDROGENATED PRODUCT			
		3 hr	6 hr	8 hr	12 hr
Sp. gr.	0·959	0·931	0·929	0·919	0·910
Tar acids, vol. %	20	11·2	5·6	4·8	3·8
up to 200°C., vol. %	..	12	12	13	15
up to 250°C., vol. %	10	32	29	33	36
up to 300°C., vol. %	70	78	71	73	76
Paraffines and naphthenes, vol. %	12·9	27·5	28·8	29·9	31·2
Olefins, vol. %	10·1	4·0	3·0	2·4	2·5
Aromatic hydrocarbons, vol. %	57·0	57·3	62·6	62·9	62·5
Sulphur, wt %	0·41	..	0·19	0·16	0·11
Nitrogen, vol. %	0·69	..	0·50	0·48	0·40

the quality of product. The tar acid content of rehydrogenated product was 8·6 per cent as compared to 14·5 vol. per cent in the once hydrogenated product.

The product in all these cases is not completely refined of tar acids since it is already known that a higher temperature is required for the complete hydrogenation of tar acids. In the experiments on continuous bench-scale unit, the product was obtained completely free of tar acids when the temperature of hydrogenation was 425-450°C.

TABLE 3—PROPERTIES OF CATALYST

(Pressure, 900 psi; Temp., 350°C.; Catalyst concentration, 20%; Duration, 3 hr)

	RAW OIL	PRODUCT WITH				
		Fresh catalyst	Once used catalyst	Twice used catalyst	Thrice used catalyst	Four times used catalyst
Sp. gr.	0·961	0·932	0·923	0·915	0·912	0·914
Tar acids, vol. %	20	10·8	8·4	6·0	5·6	5·6
Product boiling up to						
200°C., vol. %	..	5	9	10	12	11
250°C., vol. %	10	23	29	34	35	33
300°C., vol. %	70	73	77	78	80	78
Paraffins and naphthenes, vol. %	12·9	24·7	27·6	31·0	31·2	31·4
Olefins, vol. %	10·1	3·8	3·4	2·7	2·4	2·4
Aromatic hydrocarbons, vol. %	57·0	60·6	60·6	60·3	60·8	60·6

TABLE 4—REHYDROGENATION OF HYDROGENATED PRODUCT WITH FRESH AND USED CATALYSTS

(Temp. 350°C.; Pressure, 900 psi; Duration, 3 hr; Catalyst concentration, 5%)

	ONCE HYDROGENATED PRODUCT	REHYDROGENATED PRODUCT WITH FRESH CATALYST	REHYDROGENATED PRODUCT WITH USED CATALYST
Sp. gr.	0·936	0·924	0·930
Tar acids, vol. %	14·5	8·6	9·5
Product up to			
200°C., vol. %	6	12	9
250°C., vol. %	23	30·8	24·8
300°C., vol. %	70·5	73·5	72·4
Paraffins and naphthenes, vol. %	22·7	26·7	24·9
Olefins, vol. %	2·7	2·3	2·9
Aromatic hydrocarbons, vol. %	60·1	62·4	62·7

EXPERIMENTS IN THE CONTINUOUS BENCH-SCALE UNIT

A bench-scale unit with a fixed bed of pelletized catalyst (60 ml.) was used for these investigations. The experimental set-up consisted of a reactor of special steel, 1 metre long and 12 mm. internal diam. The reactor was surrounded by a steel block furnace which was heated by two heating coils, one of which was connected to the temperature controller. The temperature could be maintained at any desired level by means of this arrangement. The catalyst bed was taken in the middle section of the reactor between two portions of inert material.

Hydrogen from a high pressure cylinder and tar oil fraction by means of an Andreas Hofer high pressure liquid pump were fed from the top. The fraction boiling between 220° and 290°C. was used as the feed. The products were cooled and gaseous products were separated from liquid product. The rate of liquid feed was regulated by means of an adjustment in the pump, while the rate of gas flow was controlled by means of needle valve after the separator. The gas rate was measured by means of wet gas meter. At the end of the experiment, the product was collected after cooling and releasing the pressure, and analysed according to standard methods.

The four variables that can influence the hydrogenation process are temperature, pressure, rate of oil feed and ratio of oil/hydrogen. Earlier experiments with the neutral oil from this tar fraction and with a different tar fraction showed that the hydrogen/oil ratio has title influence on the hydrogenation[4,5]. In large-scale practice the rate of gas flow is not usually altered. Any desired change in the product is achieved by altering the temperature, pressure or space velocity of feed. Consequently in the present experiments also only these three variables were altered. The ratio of hydrogen/oil was maintained in all the experiments between 500 and 600.

Influence of Temperature. At a total pressure of 70 kg./sq. cm. and a space velocity of 1 V/V/h., the temperature of hydrogenation was varied between 300 and 480°C. The results are shown in Table 5. The feed oil has a tar acid content of 23·8 per cent by volume and a tar base content of 5·7 per cent by weight. The tar acids in the product remain nearly the same at a temperature of 300°C. and begin to decrease from 350°C. onwards. At 450°C. they are completely removed. A temperature of 350°C. is sufficient to reduce the sulphur to less than 0·1 per cent from 0·41 per cent. The product is not completely free of nitrogen compounds. The product obtained at 340°C. contains 0·34 per cent of nitrogen. The volume per cent of product boiling below 200°C. increases with the temperature of hydrogenation. The aniline point of the product boiling above 200°C. increases with increasing temperature of hydrogenation up to 425°C. and then begins to decrease. The volume of saturated hydrocarbons (in the total product) is also maximum at 450°C.

TABLE 5—INFLUENCE OF TEMPERATURE OF HYDROGENATION

(Pressure, 70 kg./sq. cm.; Space velocity, 1 V/V/h.)

	Feed oil	Product					
Temp. of hydrogenation, °C.		300	350	400	425	450	480
Sp. gr. of total product	0·9552	0·9482	0·9279	0·9025	0·8805	0·8743	0·8775
Sp. gr. of fraction boiling between 0 to 200°C.	..	..	..	..	0·8098	0·8063	0·8106
Sp. gr. of fraction boiling between 200 and 340°C.	..	0·9361	0·9236	0·9082	0·8965	0·8940	0·9087
Tar acids, vol. %	23·8	23·2	17·8	8·4	0·3	traces	traces
Tar bases, wt %	5·7	4·3	2·9	2·9	2·2	2·9	2·5
Sulphur, wt %	0·41	0·38	0·09	0·08	0·03	0·03	0·06
Distillation							
10 vol. % at, °C.	235	223	220	200	164	150	122
50 do	266·5	264	262	256	252	246	233
90 do	326·5	323	331	318	315	309	308·5
Fraction up to 200°C., vol. %	..	1·0	3	10	21·5	26	33·5
Aniline point 200-340°C. fraction, °C.	18·8	16·2	22	22·3	25·7	24	17·8
Hydrocarbon Type Analysis							
Aromatics, vol. %	39·6	48·9	50·8	54·1	60·4	59·3	62·4
Olefins, vol. %	12·3	5·2	4·7	1·6	0·9	0·8	0·8
Saturated hydrocarbons, vol. %	18·6	18·4	23·8	33·0	36·3	37·0	34·3

Influence of Pressure. The pressure of hydrogenation was increased from 30 atm. to 120 atm. at a temperature of 450°C. and a space velocity of 1 V/V/h. An increase in pressure will increase the time of contact of the reactants which in turn will improve the quality of product. This is substantiated by the results obtained (Table 6). It is seen that with increasing pressure, the tar bases content decreases; the aniline point of product boiling above 200°C. increases. The volume of product boiling above 200°C. decreases. The hydrocarbon type analysis shows that the content of staturated hydrocarbons increases to 43 per cent at a pressure of 120 kg./sq. cm.

Influence of Space Velocity. With increasing rate of feed the contact time is decreased and this has an unfavourable effect on the hydrogenation (Table 7). In this series of experiments the space velocity was increased from 0·42 to 3·66, keeping the temperature at 450°C. and pressure at 70 kg./sq.cm.

TABLE 6—INFLUENCE OF PRESSURE OF HYDROGENATION

(Temp., 450°C.; Space velocity, 1 V/V/h.)

	Feed	Pressure, kg./sq.cm.				
		30	50	70	100	120
Sp. gr. of total product	0·9552	0·9047	0·8855	0·8743	0·8586	0·8574
Sp. gr. of 0-200°C. fraction	..	0·8408	0·8192	0·8063	0·8000	0·7969
Sp. gr. of 200-340°C. fraction	..	0·9137	0·9022	0·8940	0·8824	0·8837
Tar acids, vol. %	23·8	2·4	0·6	..	traces	..
Tar bases, wt %	5·7	4·7	2·8	2·9	1·6	1·1
Sulphur, wt %	0·41	0·12	0·01	0·03	..	..
Distillation						
10 vol. % at, °C.	235	178	153	150	138	144
50 do	266·5	253·5	248·5	246	243	241·5
90 do	326·5	316	312·5	309	313	308
Fraction up to 200°C., vol. %	..	17·2	24	26	30	29
Aniline point of 200-340°C. fraction	18·8	20	22·6	24	29·3	29·3
Hydrocarbon Type Analysis						
Aromatics, vol. %	39·6	67·1	60·7	59·3	53·8	54·1
Olefins, vol. %	12·3	0·7	1·5	0·8	1·3	1·2
Saturated hydrocarbons, vol. %	18·6	25·1	34·4	37·0	43·3	43·3

TABLE 7—INFLUENCE OF SPACE VELOCITY
(Pressure, 70 kg./sq. cm.; Temp., 450°C.)

Space velocity, v/v/h.	Feed oil	0·41	1	1·45	1·95	2·73	3.66
Sp. gr. of total product	0·9552	0·8703	0·8870	0·8940	0·9070	0·9149	0·9212
Sp. gr. of 0-200°C. fraction	..	0·8016	0·8164	0·8200	0·8225	..	..
Sp. gr. of 200-340°C. fraction	..	0·8951	0·9050	0·9089	0·9156	0·9171	0·9254
Tar acids, vol. %	23·8	..	..	traces	6·8	10·8	12·8
Tar bases, wt %	5·7	4·9	5·1	4·9	4·3	4·9	5·9
Sulphur, wt %	0·41	0·07	0·09	0·07	0·10	0·16	0·24
Nitrogen, wt %	0·61	0·26	0·35	0·30	0·28	0·35	0·45
Distillation							
10 vol. % at, °C.	235	142	166	168·5	191	208·5	212
50 do	266·5	245	250	253·5	255	260	261
90 do	326·5	317	316	313	319	325	327
Fraction up to 200°C. ,vol. %	..	27·5	20·5	18·5	12	8	7·5
Aniline point of 200-340°C. fraction, °C.	18·8	25·0	22·8	22·2	21·3	19·2	17·5
Hydrocarbon Type Analysis							
Aromatics, vol. %	39·6	57·5	57·6	58·6	58·4	52·0	51·6
Olefins, vol. %	12·3	1·0	1·0	1·3	2·6	4·9	5·1
Saturated hydrocarbons, vol. %	18·6	36·6	36·2	35·2	27·9	27·4	24·6

With increasing space velocity the tar acids are not completely hydrogenated. Consequently the aniline point of product boiling above 200°C. decreases as also the percentage of saturated hydrocarbons. A space velocity of about 1·5 appears to be optimum for the complete removal of tar acids. At this feed rate about 83 per cent of sulphur and about 50 per cent of nitrogen are removed.

Activity of Catalyst. The catalyst was found to be active even after about 100 hours of operation. The only difficulty encountered was due to polymerization and coke formation in a portion of the reactor where cold feed entered. This can be overcome by pretreating the feed-stock with hydrogen at a much lower temperature.

The results presented here were recorded when steady conditions in the catalyst activity were reached. However, it was found that the fresh catalyst had a better activity as shown by tar bases removal and the fraction of product boiling below 200°C. The results obtained at a temperature of 450°C., at a pressure of 50 kg./sq.cm. and at a space velocity of 1 v/v/h. are reported in Table 8. The catalyst contains about 5 per cent silica. It is probable that the acidic centres of the catalyst become poisoned with the tar bases or their decomposition product, ammonia and this leads to loss of activity with regard to further removal of tar bases and also to a reduction in the fraction boiling below 200°C. This needs further confirmation.

TABLE 8—PRODUCT OBTAINED WITH FRESH AND USED CATALYSTS

(Pressure, 50 kg./sq. cm.; Temp., 450°C.; Space velocity, 1 v/v/h.)

	PRODUCT OBTAINED WITH	
	Fresh catalyst	Used catalyst (after about 40 hrs)
Sp. gr. of total product	0·8633	0·8855
Sp. gr. of 0-200°C. fraction	0·8120	0·8192
Sp. gr. of 200-340°C. fraction	0·8902	0·9022
Tar acids, vol. %	traces	traces
Tar bases, wt %	0·87	2·84
10 vol. % at, °C.	117·5	153
50 do	232·5	248·5
90 do	301	312·5
Fraction up to 200°C., vol. %	35	24
Hydrocarbon Type Analysis		
Aromatics, vol. %	61·3	60·7
Olefins, vol. %	0·9	1·5
Saturated hydrocarbons, vol. %	36·9	34·4

Product Utilization. The 200-340°C. fraction of product has a maximum aniline point of about 29°C. and as such does not meet the specifications for diesel oil. Further processing by solvent extraction will yield a product with higher aniline point. Hydrogenation at still higher pressures may give a more saturated product but the economics of the process will be unfavourable. The neutral oil from the same tar oil fraction yields a product with a higher aniline point under the same conditions of hydrogenation.

TABLE 9—HYDROGENATION OF NEUTRAL OIL AND WHOLE TAR OIL FRACTIONS AND A TAR FRACTION FROM UPPER KAJORA TAR AND NEUTRAL OIL FRACTION THEREOF

	KOTHAGUDEM COAL		UPPER KAJORA COAL			
	Tar fraction (B.P. 220-290°C.)	Neutral oil thereof	Tar fraction (200-300°C.)		Neutral oil thereof	
			Feed	Product	Feed	Product
Temperature, °C.	450	450	..	460	..	450
Pressure, kg./sq.cm.	70	70	..	70	..	50
Sp. gr. of total product	0·8743	0·8604	0·952	0·8616	0·8722	0·8476
Sp. gr. of 0-200°C. fraction	0·8062	..	..	0·8390	..	..
Sp. gr. of 200-340°C.	0·8940	0·8729	..	0·8840	..	0·8524
Tar acids, vol. %	traces	..	45·0	3·0	..	..
Tar bases, wt. %	2·9	..	0·45	1·33	..	..
Distillation						
10 vol. % at, °C.	150	188	198	132	203	172
50 ,,	246	256	231	205	252	242
90 ,,	309	311	293	284	308	302
Fraction up to 200°C., vol. %	26	13	..	47	9	23
Aniline point of 200-340°C., fraction °C.	24	37·6	..	34·0	32·0	48·0
Sulphur, wt %	0·03	0·08	0·20	..	0·32	0·03
Hydrocarbon Type Analysis						
Aromatics, vol. %	59·3	50·0	24·9	51·2	46·0	43·0
Olefins, vol. %	0·8	0·8	15·0	0·6	27·0	0·7
Saturated hydrocarbons, vol. %	37·0	49·2	15·6	43·9	27·0	56·3

The results obtained with neutral oil are given in Table 9. For comparison the data obtained by the hydrogenation of l. t. tar fraction from Upper Kajora non-caking coal are also included[5].

It is seen that the neutral oil from the tar fraction obtained from Kothagudem coal gives a more saturated product on hydrogenation than the tar fraction with tar acids and tar bases. It may be worth considering separation of tar acids prior to hydrogenation. The product of hydrogenation of tar fraction from Upper Kajora coal gives a product with an aniline point of 34°C. although the tar fraction contains 45 per cent (by volume) of tar acids. In this case, the volume of product boiling below 200°C. is as high as 47 volume per cent. The neutral oil from the fraction gives on hydrogenation a product with an aniline point of 48°C.

The portion of product boiling below 200°C. may find ready market as solvent for rubber, varnishes, etc. or as raw material for chemical industry.

COLCLUSION

The l. t. tar fraction with a boiling range of 225-290°C. obtained from carbonization of non-caking coal from Kothagudem coal can be satisfactorily hydrogenated at a temperature of 425-450°C. and under medium pressures to a product free from tar acids and sulphur compounds. The product, however, appears to be not quite suitable for use as diesel fuel as such. The neutral oil from this fraction gives a product that may find use as diesel fuel after some treatment.

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Utilization of Low Temperature Tar

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Extraction studies of tar acids using different solvents and processes developed for utilization of tar acids are reported. Methods for utilization of tar bases are indicated. Studies on hydrogenation of neutral oil fractions and cracking of higher boiling fractions are also reported. A scheme for the complete utilization of low temperature tar is presented.

Low temperature carbonization (l. t. c.) of coal aims primarily at the production of soft coke for domestic use. However, gas, light spirit, tar and liquor are also produced in the process as byproducts. The composition of tar produced by this process is different from that by the high temperature process and so the conventional scheme of treatment adopted for tar from high temperature carbonization is not applicable to low temperature (l. t.) tar.

The necessity of putting up l. t. c. plants in this country is now realized and it is anticipated that commercial units will be installed in the country in the near future. The installation and operation of the two pilot plants—one at Regional Research Laboratory (RRL), Hyderabad, and the other at Central Fuel Research Institute (CFRI), Jealgora, are rather significant in the above context.

Since the production of soft coke and processing of byproducts are very much interconnected, investigations on the utilization of l. t. tar would be very useful in the planning of the l.t.c. industry. The results of some of the important investigations carried out at CFRI in relation to the proposed plan of utilization of l.t. tar are, therefore, reviewed in this paper.

By distillation and suitable extraction tar samples are separated into tar acids, tar bases, and neutral oil, which are then investigated as follows:

TAR ACIDS

Extraction of Tar Acids. Tar acids constitute 20-30 per cent of l. t. tar and are in much demand for their varied uses. Efficient extraction and utilization of these constituents, therefore, contribute very significantly to the economics of the l. t. c. industry.

The conventional process of alkali extraction has a number of obvious disadvantages and, hence, research on the development of improved techniques like liquid-liquid extraction, azeotropic distillation, etc. with one or more of organic solvents like, methanol, "Metasolvan" (70 per cent aqueous methanol), ethanolamine, organic esters, ethers, ketones, fatty acids, etc. has been in progress in different countries. Three processes of this type have been developed and are being further investigated at CFRI.

The first is based on the fact that acidamides and thioamides, specially urea and thiourea, form loose addition compounds or adducts with tar acids. These adducts can be separated as crystals, purified and decomposed by heat or solvent extracted to liberate the tar acids in a pure form. The process has been tried successfully for a number of simple phenols. The presence of pyridine bases affects the efficiency of the process and hence, bases should preferably be removed beforehand. The applicability and efficiency of the process with respect to more complex phenols are being investigated[1].

In a second process dilute acetic acid is used as the extracting medium. Coal tar fraction up to 270°C. has been used and the effect of variation of temperature, tar oil/solvent ratio and strength of the solvent has been studied in detail. The best results are obtained with 60 per cent acetic acid using a ratio of 0·8 part of solvent to 1 part of oil at a temperature of 20-25°C. The recovery and purity of the tar acids under these conditions are 89·45 and 71·63 per cent respectively in two extractions. In order to remove the neutral constituents carried over, the extract is further washed with solvents like n-hexane, n-heptane or petroleum fractions. Best results are obtained by washing with petroleum fractions. The tar acids and the solvent can be separated by fractionation. Purity of the final products is of the order of 90-95 per cent.

Tables 1 and 2 illustrate the effect of variation of the strength of solvent and the ratio of tar oil to solvent. Temperature has little or no effect on the extraction efficiency[2].

The third process for the tar acid extration under investigation is a two stage one. In the first stage an organic amine like monoethanolamine or ethylene diamine is used for extracting the acids from the tar distillates and aqueous liquor. In the second stage, the extract from the first stage is treated with a suitable compound of the type of an organic ester, ether or ketone, to separate again the tar acids from the solvent of the first stage. The final recovery of the tar acids is achieved by distillation. All the solvents

TABLE 1—EXTRACTION OF TAR ACIDS FROM CRUDE TAR OILS—EFFECT OF VARIATION OF STRENGTH OF SOLVENT

(Feed, l.t. tar oil fraction up to 270°C.; Solvent, acetic acid; Feed: Solvent ratio = 1 : 1)

Strength of solvent % w/w	Recovery of fractions in one extraction						Recovery of fractions in two extractions					
	Tar acids		Bases		Neutral oils		Tar acids		Bases		Neutral oils	
	Wt of tar acids*	% recovery	Wt of bases*	% recovery	Wt of neutral oils*	% recovery	Wt of tar acids*	% recovery	Wt of bases*	% recovery	Wt of neutral oils*	% recovery
30	4·51	9·96	0·30	6·56	0·30	0·59	5·25	11·60	0·70	15·49	5·69	11·31
40**	..	..	..	..	..	..	..	..	..	..	..	..
50	27·64	61·05	2·17	48·16	5·46	10·85	33·79	74·64	2·70	57·23	7·12	14·15
60	37·48	82·79	4·08	90·55	8·74	17·37	41·60	91·89	4·37	96·99	10·25	20·36
70	37·36	92·52	4·31	95·66	13·63	27·08	40·35	89·13	4·51	100·00	15·59	30·97
80	39·06	86·30	4·21	93·35	16·51	32·81	41·07	90·72	4·51	100·00	19·09	37·93

*Basis 100 g. tar oil feed. ** Separated into three phases.

TABLE 2—EXTRACTION OF TAR ACIDS FROM CRUDE TAR OILS—EFFECT OF VARIATION OF TAR OIL/SOLVENT RATIO

[Feed, l.t. tar oil fraction up to 270°C.; Solvent, acetic acid; Strength of solvent (% w/w), 60]

Feed solvent ratio	Recovery of fractions in one extraction						Recovery of fractions in two extractions					
	Tar acids		Bases		Neutral oils		Tar acids		Bases		Neutral oils	
	Wt of tar acids*	% recovery	Wt of bases*	% recovery	Wt of neutral oil*	% recovery	Wt of tar acids*	% recovery	Wt of bases*	% recovery	Wt of neutral oils*	% recovery
1 : 1	37·48	82·79	4·08	90·55	8·74	17·37	41·60	91·89	4·37	96·99	10·25	20·36
1 : 0·8	36·32	80·23	4·17	92·53	10·27	20·40	40·49	89·45	4·44	98·54	11·61	23·08
1 : 0·6	36·53	80·71	3·81	84·47	8·28	16·45	38·32	84·65	4·01	88·90	9·67	19·22
1 : 0·5	35·71	78·89	3·64	80·78	11·10	22·06	38·89	85·90	..	..	..	..
1 : 0·4**	..	..	..	..	..	..	..	..	..	..	..	..

*Basis 100 g. tar oil feed. ** Separated into three phases.

are recycled and mutual solubility being of a low order, the loss of solvents is insignificant. The efficiency of extraction at the two stages are 95 and 80 per cent respectively and the purity achieved is more than 95 per cent. Schematically the process is represented in Fig. 1 and examples and extraction efficiency[3] are given in Table 3.

Utilization of Tar Acids. Low boiling phenols are in sufficient demand in industries manufacturing plastics, medicines, antiseptics, dyes, perfumes, etc. It is the tar acids boiling above 220°C. that call for suitable methods of utilization, as excepting for a few compounds like the naphthols, catechol, resorcinol, pyrogallol, etc. most of them are not in much demand. Separation of the higher fraction into its constituents is also a costly operation. Yet this higher boiling fraction constitutes 50 to 70 per cent of the total tar acids recoverable from l. t. tar. Investigations were therefore undertaken to evolve and assess methods for their utilization.

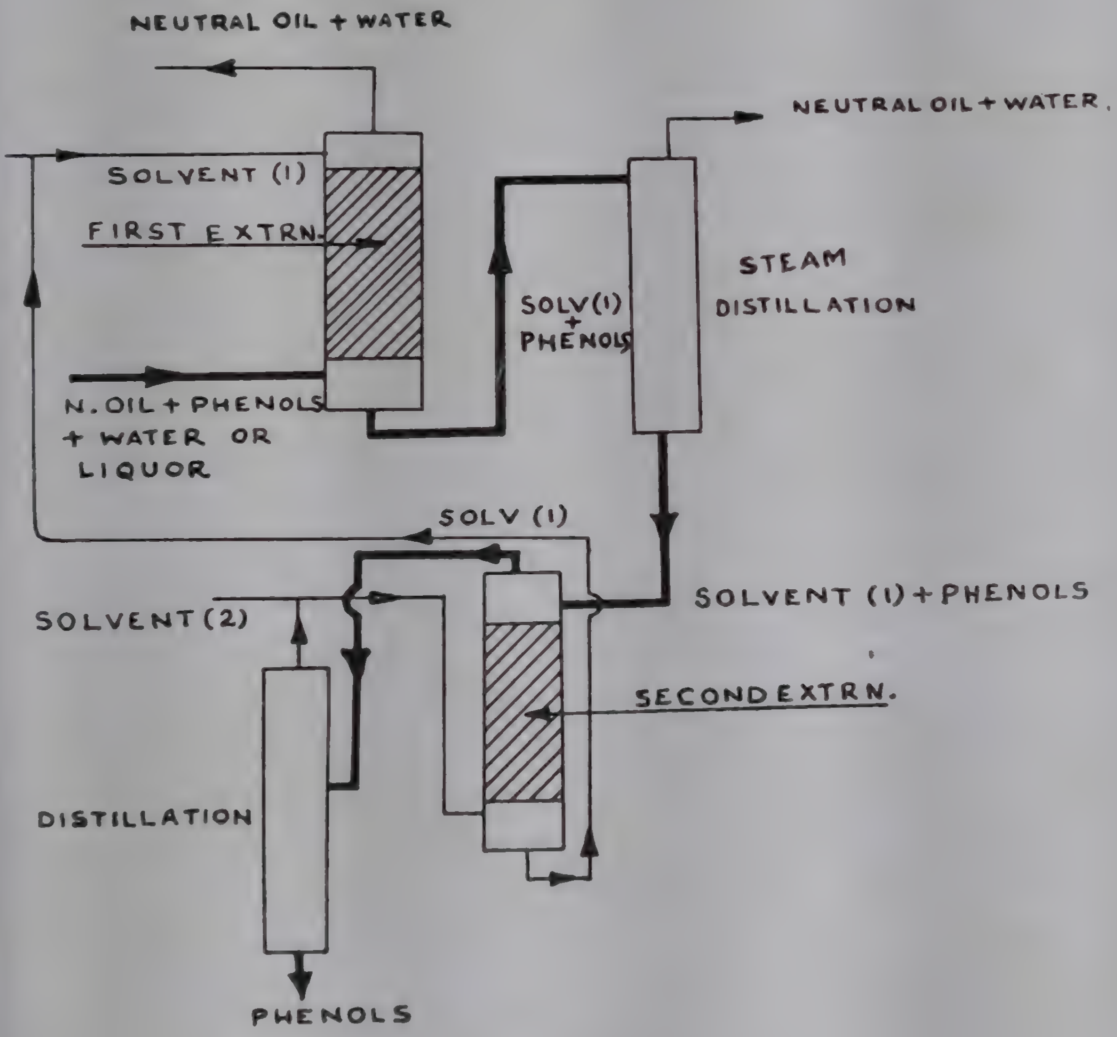
NEUTRAL OIL + WATER
NEUTRAL OIL + WATER.
SOLVENT (1)
FIRST EXTRN.
SOLV(1) + PHENOLS
STEAM DISTILLATION
N. OIL + PHENOLS + WATER OR LIQUOR
SOLV (1)
SOLVENT (2)
SOLVENT (1) + PHENOLS
SECOND EXTRN.
DISTILLATION
PHENOLS

Fig. 1—Two-stage extraction of phenols

TABLE 3—TWO-STAGE PROCESS FOR PHENOL EXTRACTION

Stage	Feed	Solvent	Feed : Solvent	No. of extractions	% of phenol extracted
1	L.T.N. oil —75% phenol —25%	Monoethanolamine + water (70 : 30)	1 : 1	1	90
1	do	Ethylenediamine + water (70 : 30)	1 : 1	1	94
2	Phenol in ethylenediamine (1 : 4)	Butyl acetate	1 : 2	2	86·8
2	do	do	do	3	91·0
2	do	do	1 : 1	3	86·1

TABLE 4—PROPERTIES OF HARD BOARD PREPARED BY THE CFRI PROCESS

	Board by CFRI process	B. S. 1142 specification for similar material
Mean density, lb./cu. ft	78·5	above 50
Modulus of rupture, lb./sq. in.	3339 (thickness 0·2 in.)	3580 (thickness 0·1875 in.)
Water absorption in 24 hr, %	17·9	30

Attention was naturally drawn at the outset towards conversion of the higher acids to lower ones, as has been attempted elsewhere. The process of hydrogenolysis has been preferred to simple cracking and catalysts like cobalt molybdate and iron chromate have been studied with wide variations of operating conditions like hydrogen pressure, temperature, duration, addition of diluents, etc. It has been observed, that the nature of hydrogenolysis, whether it is at C-C linkage or at the C-O linkage depends largely on the catalysts used, which thus appear to be quite specific in their action. Cobalt catalyst, for example, favours C-C disruption. With this catalyst, a conversion of 40-50 per cent is achieved at 50 kg./sq. cm. hydrogen pressure (cold), 400°C. and 1 hr reaction time. The product so obtained has been analysed by the counter-current distribution technique followed by u.v. absorption spectroscopy and is found to contain above 50 per cent of phenol[4].

Another method of utilization developed at this Institute consists in preparing a water soluble resin, by reacting an alkali solution of the acids with formaldehyde in the usual way[5]. The resin solution so obtained has satisfactory keeping quality and is very convenient for preparation of hard boards or bonded materials[6]. For this purpose, the resin is precipitated from the alkali solution by means of acid or salts of ammonia or alum into fibrous or powdery industrial wastes and the mixture is then processed into moulds like any other thermosetting plastic. The products are hard, water resistant and possess desirable properties. The test results of a sample prepared by this process are compared with the B.S. specifications in Table 4.

The process can be applied to the entire tar acid stock as may be obtained by alkali extraction of the total tar distillate or the fraction of boiling range 220-270°C. The fraction boiling above 270°C. is not considered suitable for the purpose.

TAR BASES

L. t. tar does not contain bases in higher concentration than high temperature tar. But as the yield of tar in l. t. c. is 3-4 times that in the high temperature process, total tar base yield by l. t. c. is much higher. An appreciable demand exists for the bases, as besides being used as solvents, compounds like pyridine, quinoline, isoquinoline and their homologues are used for a wide variety of organic preparations as medicines (antituberculosis drugs, like INH, antimalarials, antispasmodics, etc.), antiseptics, special dyestuffs (quinoline cyanine dyes), fungicides, etc.

Little was, however, known until very recently about the composition of l. t. tar bases. At CFRI, studies on the estimation of these constituents by infrared spectroscopy have been conducted[7]. The tar samples were obtained by carbonization of coal in an electric oven at 600°C. The bases were extracted in the usual way and fractionated into two fractions (0-270°C. and 270-300°C.) which were studied separately. The presence of 29 compounds in the lower boiling fractions and 18 in the higher fractions were confirmed. It has been observed that l. t. tar bases are mostly alkyl substituted pyridines and quinolines and that more complex bases like acridine, phenanthridine, benzoquinoline, etc. are practically absent.

Other studies with tar bases consist of a process for catalytic vapour phase oxidation for converting them to acids. Substances like β-picoline, γ-picoline, etc. could be oxidized to an extent of 25-30 per cent with complete recovery of the unchanged material (Table 5)[8]. A process for liquid phase oxidation of the β-picoline cut fraction has also been developed[9].

NEUTRAL OIL

Neutral oil from l. t. tar is different in composition from that of h. t. tar. It is less aromatic and contains very little naphthalene and anthracene and more of paraffinic and naphthenic bodies. Thus the method of its utilization also would be different. Although an appreciable portion of neutral oil may be processed into diesel oil by straight distillation, this can be better utilized by hydrogenation. Considerable work has been done at the Institute on this aspect.

TABLE 5—OXIDATION OF GAMMA AND BETA-PICOLINE IN FLUIDIZED CATALYTIC BED—A TYPICAL RUN

[Vol. of V_2O_5 catalyst used, 60 ml. (140 g.); Feed rate, 1·5 ml./hr; Duration of run, 3 hr]

Base	Oxidation temperature, °C.	Yield of oxidized product g.	Conversion %	Melting point of product* °C.	Unconverted base recovered	Base unaccounted for (by diff.) %	Yield**
γ-Picoline	400	1·7	28·6	310	40	31·4	9·45
β-Picoline	452	1·5	25·2	297	60	14·8	8·30

*Melting points of pure nicotinic and isonicotinic acids are 297° and 311°C. respectively.
**Yield in g./litre of catalyst/hr of run.

TABLE 6—HYDROGENATION OF L. T. TAR OIL IN BATCH PROCESS

	Upper Kajora neutral tar oil (200-250°C.)		Upper Kajora neutral tar oil (250-300°C.)		Upper Kajora neutral tar oil (300-350°C.)	
	Feed stock	Product	Feed stock	Product	Feed stock	Product
Temp., °C.	..	400	..	400	..	400
Initial H_2 pressure, kg./sq. cm.	..	100	..	100	..	100
Reaction pressure, kg./sq. cm.	..	220	..	220	..	225
Reaction time, hr	..	3	..	3	..	3
Product obtained, % (v)	..	92	..	87·5	..	87·0
Fraction up to 200°C., % (v)	..	47·5	..	18·2	..	10·8
Residue and loss, % (v)	..	4·5	..	8·7	..	16·6
Fraction 200-350°C., % (v)	..	48·0	..	73	..	72·6
Properties of oil boiling between 200-350°C.						
Aniline pt, °C.	25·6	54·0	26·8	54·6	37·2	44·6
Saturates, %	11·0	82·0	3·9	74·0	23·0	60·0
Unsaturates, %	17·5	2·0	12·0	2·0	24·0	4·0
Aromatics, %	71·5	16·0	84·0	24·0	52·0	36·0
Sp. gr. (60°F.)	..	0·84	..	0·854	..	0·89
Diesel index	..	48·0	..	45·0	..	30·8

Hydrogenation experiments have been carried out both in an autoclave and in a continuous bench-scale reactor[10]. Various catalysts have been tried and an efficient and active catalyst has been developed. It has been observed that in the batch process, fractions boiling in the ranges 200-250°C. and 250-300°C. can be converted to diesel type fuels using a catalyst at 4 per cent concentration, a temperature of 400°C., 226 kg./sq.cm. working pressure (hydrogen) and 3 hours reaction time. A Ni-Al catalyst has also been found to be satisfactory for the fraction 250-300°C. at 10 per cent concentration, 400°C., 253·3 kg./sq.cm. pressure and 5 hours reaction time. Quality, yield of the product and other data are summarized in Table 6. In the continuous process, a low pressure of 50 kg./sq.cm. has been found to be adequate but diesel oil of inferior quality corresponding to low speed diesel oil has been produced. The product can, however, be improved by removing the aromatics by solvent extraction (Table 7).

The 300-350°C. fraction has been, however, found unsuitable for conversion to diesel oils as improvement in diesel index is insignificant on hydrogenation. In the light of these experiments, it was thought reasonable to attempt cracking of this fraction. A SiO_2-Al_2O_3 catalyst (10 per cent Al_2O_3) and an active carbon catalyst have been tried for the purpose. The distillate oils used for cracking were obtained from the Lurgi-Spuelgas l. t. c. plant at RRL, Hyderabad, and two fractions 270-300°C. and 300-360°C. have been used. The effect of reaction temperature on the yield of lower boiling products and the chemical nature of the products has been studied in detail. With 300-360°C. fraction, a good yield (up to 50 per cent of the feed) of the liquid product boiling below the I.B.P. of the feed could be obtained. With increase in reaction temperature, the yield decreases due to the formation of more of gaseous products; however, the I.B.P. of the products also decreases (Fig. 2). The aromatic content of the products

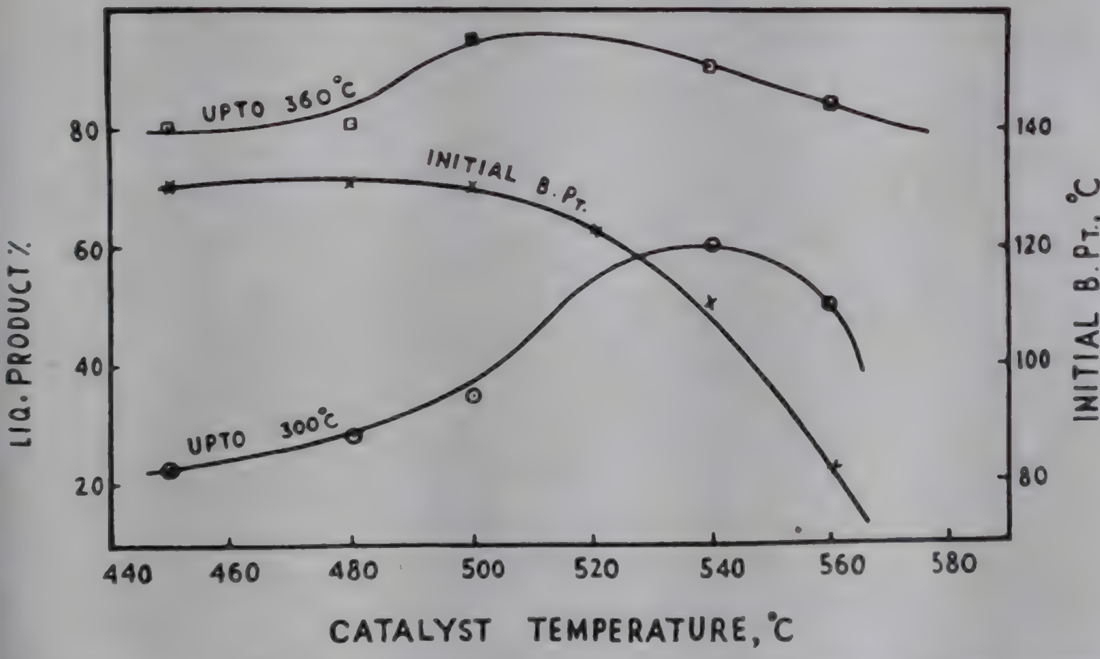

Fig. 2—Variation in yield of liquid product and I.B.P with cracking temperature

TABLE 7—HYDROGENATION OF L. T. TAR OIL IN BENCH-SCALE CONTINUOUS REACTOR

	UPPER KAJORA NEUTRAL OIL (200-250°C.)		UPPER KAJORA NEUTRAL OIL (250-300°C.)		UPPER KAJORA NEUTRAL OIL (300-350°C.)	
	Feed stock	Product	Feed stock	Product	Feed stock	Product
Experimental conditions						
Feed oil space velocity (V/V/hr)	..	0·33	..	0·575	..	0·625
Temp., °C.	..	400	..	400	..	400
Pressure, kg./sq. cm.	..	50	..	50	..	50
Rate of H_2 input, cu. ft/min.	..	0·15	..	0·115	..	0·112
Ratio of gas to oil	..	3536	..	1415	..	1267
Boiling Characteristics of Product						
Product recovered, %	..	83·0	..	83·0	..	73·0
Fraction up to 200°C., %	..	14·0	..	2·0	..	1·8
Fraction 200-350°C., %	..	81·0	..	94·0	..	80·6
Residue and loss, %	..	5·1	..	4·0	..	17·6
Properties of 200-350°C. Fraction						
Sp. gr. (60°F.)	0·876	0·870	0·934	0·903	0·968	0·952
Viscosity (Red wood 100°F.)	30·26	30·6	34·5	34·1	47·8	39·6
Flash point (P and M), °F.	150	160	174	196	142	204
Aniline point, °C.	25·6	37·4	26·8	35 6	37 2	30·8
Conradson coke	0·047	0·051	0·092	0·051	0·125	0·083
Saturates, %	11·0	45·0	12·0	34·5	23·0	27·5
Unsaturates, %	17·5	4·0	3·0	12·5	24·0	8·0
Aromatics, %	71·5	51·0	84·0	52·0	52·0	63·5
Calorific value, B.t.u./lb.	..	19,060	18,320	18,580	17,860	18,240
Diesel index	23·4	31·1	15·9	24·2	14·6	14·64

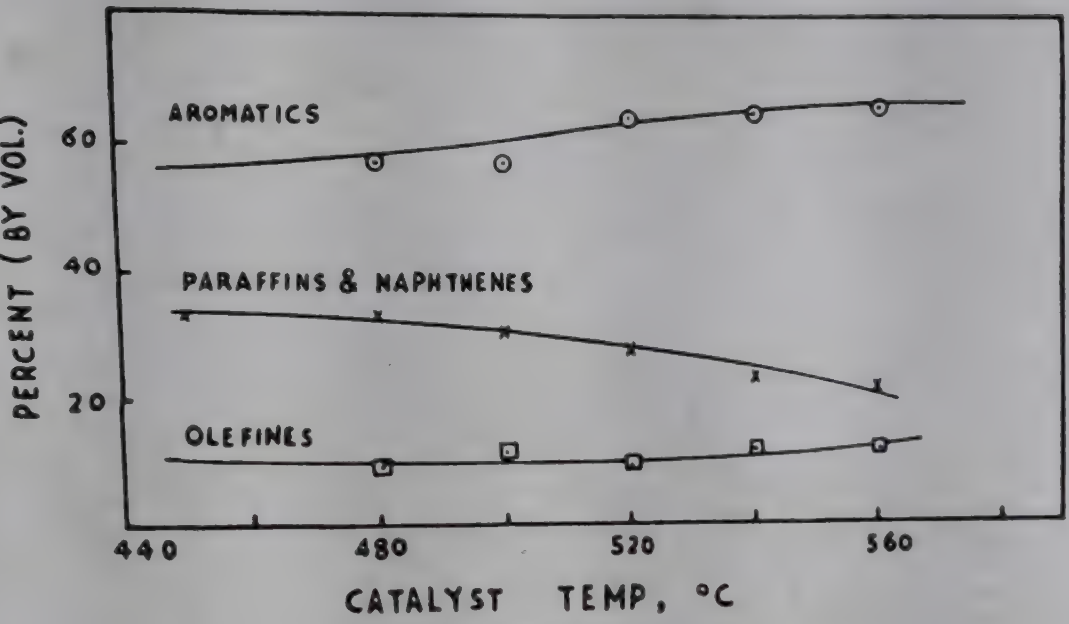

FIG. 3—NATURE OF DISTILLATE

increases steadily and the paraffins and naphthenes decrease (Fig. 3). Similar results are obtained with the fraction 270-300°C., although the yield of lighter products is less. In the case of active carbon catalyst, the conversion is less at any given reaction temperature but there is not much change in the aromatic content.

Therefore for the production of diesel type of fuel, the process of cracking alone shows no promise but it may be adopted for production of simple aromatics. The process can, however, be used along with hydrogenation for obtaining additional feed material for production of diesel type fuel from 300-360°C. fraction also[11].

CONCLUSION—A SCHEME FOR UTILIZATION

Based on the foregoing results, a scheme for complete utilization of l. t. tar has been prepared. L. t tar will first be separated into the fractions, up to 300°C., 300-360°C and pitch. The fraction 300-360°C. containing above 30 per cent tar acids may be used as such, as rot proofing agent for preservation of ropes, etc. or it may be subjected to cracking to produce simpler aromatics or a lower boiling product suitable for hydrogenation to diesel oil. Higher boiling portion from cracking may then be used for preparation of rot proofing agents or cresylic creosotes along with the higher fraction of the tar acids that may be obtained as unconverted residues from plants for conversion of higher phenols to lower ones.

The fraction up to 300°C. will be separated into neutral oil, tar acids (mostly boiling up to 270°C.) and tar bases (up to quinolines and their homologues). Neutral oil will be separated into light oil (up to 210°C.) and middle oil (210-300°C.). Light oil should be fractionated further for

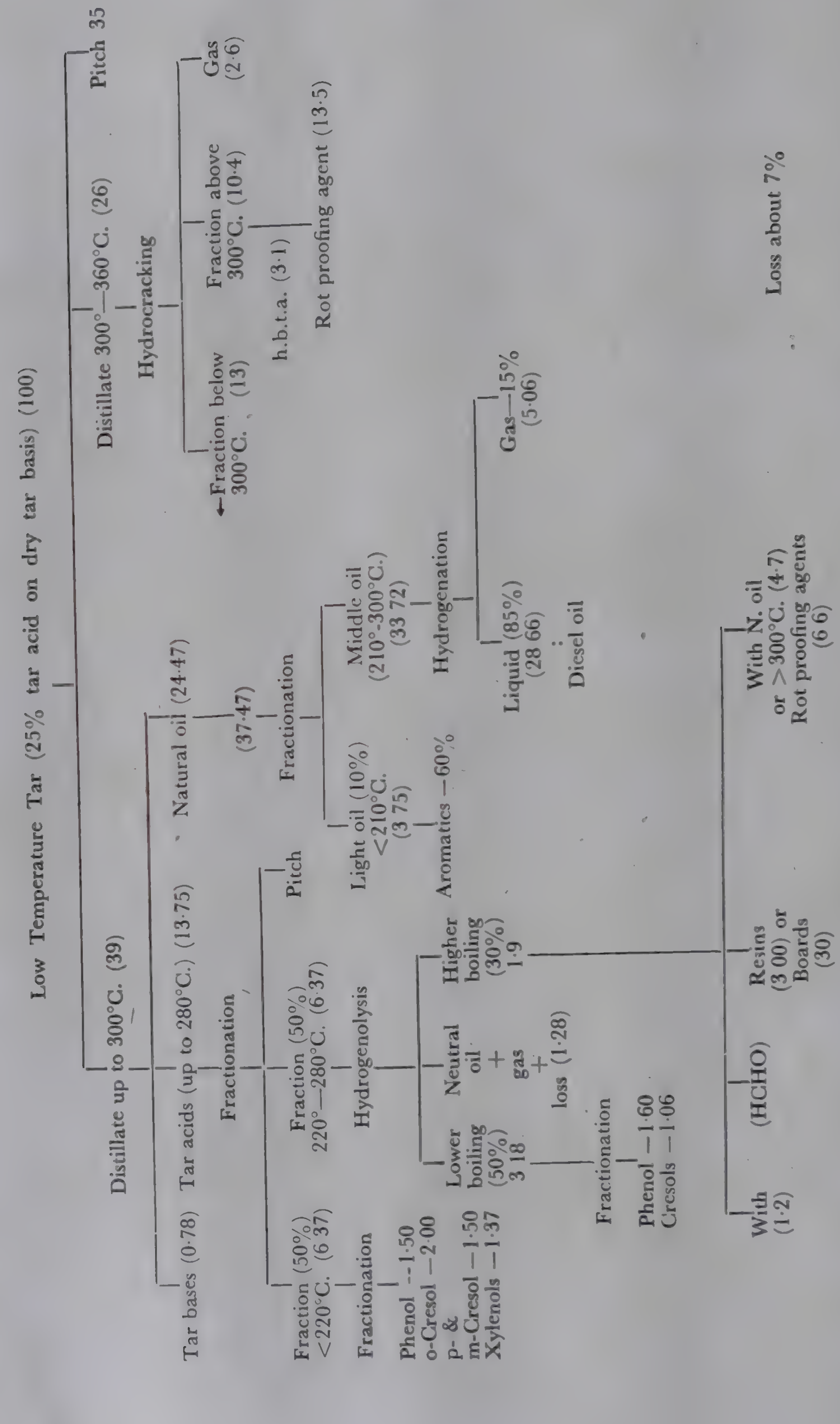
Low Temperature Tar (25% tar acid on dry tar basis) (100)
Distillate up to 300°C. (39)
Distillate 300°—360°C. (26)
Pitch 35
Tar bases (0·78)
Tar acids (up to 280°C.) (13·75)
Natural oil (24·47)
Hydrocracking
Fractionation
(37·47)
Fraction below 300°C. (13)
Fraction above 300°C. (10·4)
Gas (2·6)
h.b.t.a. (3·1)
Rot proofing agent (13·5)
Fraction (50%) <220°C. (6·37)
Fraction (50%) 220°—280°C. (6·37)
Pitch
Fractionation
Light oil (10%) <210°C. (3·75)
Middle oil (210°-300°C.) (33·72)
Fractionation
Hydrogenolysis
Hydrogenation
Phenol —1·50
o-Cresol —2·00
p- & m-Cresol —1·50
Xylenols —1·37
Lower boiling (50%) 3·18
Neutral oil + gas + loss (1·28)
Higher boiling (30%) 1·9
Aromatics —60%
Liquid (85%) (28·66)
Diesel oil
Gas—15% (5·06)
Fractionation
Phenol —1·60
Cresols —1·06
With (1·2)
(HCHO)
Resins (3·00) or Boards (30)
With N. oil or >300°C. (4·7) Rot proofing agents (6·6)
Loss about 7%

CHART I—A SCHEME FOR UTILIZATION OF LOW TEMPERATURE TAR recovery of lower aromatics (benzene, toluene, xylene, etc.) and the residue from fractionation (heavier fraction) should be cut back with the middle oil. The middle oil, together with the lighter fractions obtained from cracking of 300-360°C. fraction, will be subjected to hydrogenation to yield diesel oil (yield 85 per cent).

Tar acids (up to 270°C.) will be separated into up to 230°C. and 230-270°C. fractions. The first fraction may be further fractionated into individual phenols. The second fraction has to be subjected to hydrogenolysis. About 50 per cent of this fraction will be obtained as lower phenols which could be mixed with a lower phenol mentioned above and processed. About 30 per cent of the feed will remain high boiling which may be used either in alkali solution for the preparation of resin using formaldehyde (proportion: 2·2 parts of 30 per cent tar acids in alkali to one part of 40 per cent formaldehyde to yield 1 part of resin sufficient for 10 parts of hard board) or may be mixed with neutral oil (boiling above 300°C.) in 30 per cent concentration to produce cresylic creosotes. Alternatively, this can be further hydrogenated to lower phenols if the economics justify such a treatment. It may also be chlorinated to produce fungicides. About 10-20 per cent of the high boiling tar acids are obtained as neutral oil on hydrogenolysis, which is suitable for use as diesel oil and hence may be mixed with the products from hydrogenation of the 300-360°C. fraction. A pilot plant of 1-ton/day capacity for studies on hydrogenation of l. t. tar is being installed at the CFRI. The tar that will be produced in the prototype l. t. c. plant of the CFRI will be used for tests on this plant. The envisaged scheme of utilization is given in Chart I.

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DISCUSSION

Dr K. T. Achaya: I am rather interested in the statement that phenols form adducts with urea. As far as I know the adduct formation is limited to aliphatic compounds with more than 12 carbon atoms or aromatics with an aliphatic side chain of this length.

Dr H. S. Rao: We have tried clathrate complex formation for the separation of 2 : 6-lutidine from the 'beta-picoline cut'. These results have been incorporated in a patent. Clathrate formation is not restricted to aliphatic straight chain compounds of high molecular weight alone, but can also be applied to some other types of hydrocarbons.

Dr P. K. Banerjee: While Saha and others of our Institute were preparing for a patent on the extraction of phenols with urea solution based on their work earlier completed, Kowalsky and others published a paper on a similar process, which provided additional evidence for the basic facts behind the process of Saha and others, e.g. phenols form loose adducts with urea. [Brennstehemie., **40** (1959), 33]. The actual investigations were, however, different in these two cases. Whereas Saha worked with compositions similar to that of l.t. tar distillates, Kowalsky worked with solutions of pure phenols.

Shri Y. V. Subba Rao: As mentioned by Dr Banerjee, aqueous urea solution has also been used by Prof. Kowalsky for the extraction of tar acids from synthetic mixtures of tar acids and neutral oil; it was, however, stated that no solid adducts separated out with aqueous urea. I would like to know whether the present authors have obtained any solid adducts with tar oil distillates containing about 30 per cent tar acids.

With reference to the author's work on the use of Monoethanol amine and butyl acetate (Phenosolvan) as dual solvents for the extraction of tar acids from tar oils and aqueous liquors, I seek clarification on the following points:

1. The authors may be aware of the work by Chang and coworker [*J. Inst. Fuel*, **32,** (1959), 174; *U. S. Bureau of Mines Report of Investigation* No. 5705 (1961)] on the use of aqueous monoethanol amine and a paraffinic solvent like hexane as dual solvents for extraction of tar acids from tar oils. They reported that using 70 per cent monoethanol amine, the extraction efficiency was up to 95 per cent but the tar acids contained about 15-20 per cent neutral oil and bases; they therefore used hexane as a second solvent to improve the quality of tar acids. The work reported by the present authors recommends the use of butyl acetate (Phenosolvan) as the second solvent to extract the tar acids from the monoethanol amine extract and claimed a purity of 90-95 per cent tar acids. It is well known that butyl acetate is a good solvent for neutral oil and bases as well. I would therefore, like to know more details about the conditions used for obtaining such high purity of tar acids.

2. It is well known that monoethanol amine has infinite solubility in water. How could it be used as a solvent for extracting tar acids from aqueous liquors ? I presume that the aqueous liquor from which tar acids were to be extracted was itself used in preparing the aqueous monoethanol amine solution (which was subsequently used for extraction of tar acids from tar oil). This point also may be clarified.

Dr P. K. Banerjee: I would suggest that Shri Subba Rao and Dr Achaya may look up the paper by Prof. Kowalsky and coworkers for more details. In this paper the authors have clearly stated that addition compounds are formed as stated by us and can be obtained as 'white crystal needles' which may be kept in solution for ease of separation of extract and raffinate layers and obtained afterwards from the extract if desired. Paraffins form addition compounds with urea much more slowly and even under conditions where no such compounds can be formed, e.g. with very dilute urea solutions, phenol combines readily and with high efficiency. There is wide variation in the time taken in the formation of addition compounds with phenol and with paraffins thus making the separation easy.

Our experience regarding crystal formation of urea with phenols is similar to that of Prof. Kowalsky.

With regard to the other points raised, I may state that:

(1) The figures for monoethanol amine quoted by Shri Subba Rao from the work of Shri Chang and coworkers have actually been found to be valid by us also. Certain other organic bases gave better results as reported in our paper. The purity claimed was obtained by proper selection of the base, and incorporation of certain well known additional techniques and procedures, which are not of such special nature as to warrant mentioning. The limited scope of the paper, dealing with a number of processes simultaneously did not allow incorporation of details on these techniques.

(2) Shri Subba Rao's presumption is correct. The monoethanol amine solution is not used for extraction of tar acids from liquors exclusively.

Full details of the process and results will be published shortly in the form of a paper.

Phenol Recovery from Effluents

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The various processes for the recovery of phenols from effluent liquors are reviewed and the phenosolvan process in particular is described. The comparative advantages and disadvantages of isopropyl ether and butyl acetate as solvents are mentioned. Modifications in the process for dephenolization of coke-oven effluents are indicated.

The effluents from coking of bituminous coal, low temperature carbonization (l. t. c.) of brown coal and more recently, coking of brown coal (the so-called coke-oven effluents and carbonization liquors) contain, among others, phenols which are poisonous to fishes and other living organisms. The purification of these effluents is therefore necessary according to law.

Originally, the effluent disposal problem was solved by discharging the effluents to abandoned underground mines, ash dumps, or exhausted open-cut mines, where they were allowed to percolate. However, it was found in some cases that the effluents came back to the surface again. Another method of disposal was by the use of combustion furnaces. The effluent was sprayed into these furnaces and evaporated, the phenols and other coal byproducts being destroyed. The cost of the fuel for evaporation alone amounts roughly to DM. 6 per cubic meter of effluent, even when using a cheap type of brown coal. In addition, there are the capital charges, cost of labour and other operating expenses. These methods, as well as the biological treatment, which was initially applied in the carbonization plant at Golzau, are therefore expensive processes for destruction of phenols, which otherwise could form a valuable raw material for chemical industry.

PHENOL RECOVERY

The recovery and utilization of phenols from effluents was therefore considered as a method of disposal of the effluents.

Benzene Wash Process (Pott-Hilgenstock). The increasing gas production from bituminous coal in coke-oven plants and gasworks around the year 1920 instigated Emschergenossenschaft to develop the Pott-Hilgenstock process in which the phenols were removed from effluents by washing with benzene produced in the works. Phenols are recovered in the form of phenolates which are supplied to tar processing plants for the production of pure products. Although coke-oven effluents have a rather low phenol content of 1·5-3·0 g./litre, the cost of the process was tolerable due to the possibility of combining effluent treatment with ammonia recovery.

Oil Wash Process: Tests at Golzau and Kopsen. When in 1935 l.t.c. of brown coal increased rapidly as a result of the autarchic tendencies in Germany, a solution for the treatment of these effluents had to be found. Semi-technical tests were conducted at Golzau and Kopsen during 1938-1939 on dephenolization of waste liquors obtained from l.t.c. of brown coal, by washing with brown coal oil, based on the same principle as the Pott-Hilgenstock process for bituminous coal. Although these tests were partly successful, they did not establish a basis for construction of commercial plants, in spite of the fact that this liquor has a higher phenol content of 10-35 g./litre.

Tricresylphosphate Process: IG-Leuna. Leuna Werke developed the Tricresylphosphate process which removes the phenols from effluents from l.t.c. plants by making use of the solvent, tricresylphosphate. One disadvantage of the process is that the solvent has a higher boiling point than the extracted phenols, and the purification of the solvent to remove tarry materials is a rather difficult and costly procedure. A plant was erected at Nachterstedt, but further plants of this type were not built.

Steam Stripping Process: Koppers. In contrast to the above extraction method, Koppers developed a steam stripping process which was applied in a plant at Bohlen. The disadvantage of this process is that it permits recovery of monohydric phenols only.

Phenosolvan Process: IG/Lurgi. IG Farben and Lurgi jointly developed in 1938 the Phenosolvan process which removes the phenols from the effluents by extraction with oxygen-containing solvents, e.g. butyl acetate. This proved to be the most suitable effluent purification method both, technically and economically.

The arrangement of the process is illustrated in Fig. 1. After pre-cleaning, the effluent enters the multistage counter-current extractor in which it is treated with Phenosolvan (collective term for the solvents used) flowing in counter-current direction. The phenol content of the effluent decreases from stage to stage, and that of the extract increases accordingly. The Phenosolvan is recovered by subsequent distillation, and the extracted phenol runs off as distillation bottoms product. Similarly, the solvent contained in the dephenolized effluent (so-called weak liquor) is recovered by steam stripping.

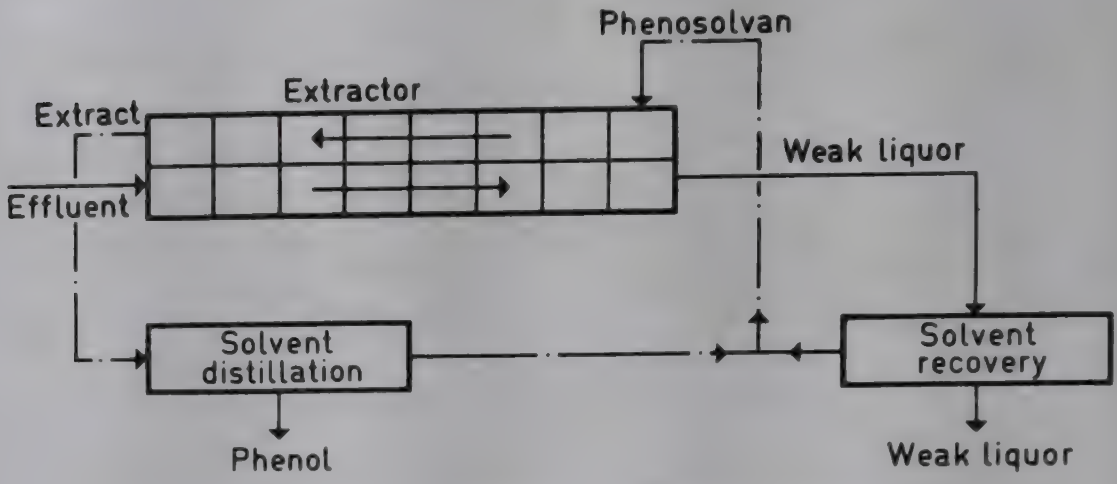
Phenosolvan
Extractor
Extract
Effluent
Weak liquor
Solvent distillation
Solvent recovery
Phenol
Weak liquor

Fig. 1—Flow diagram of Phenosolvan process

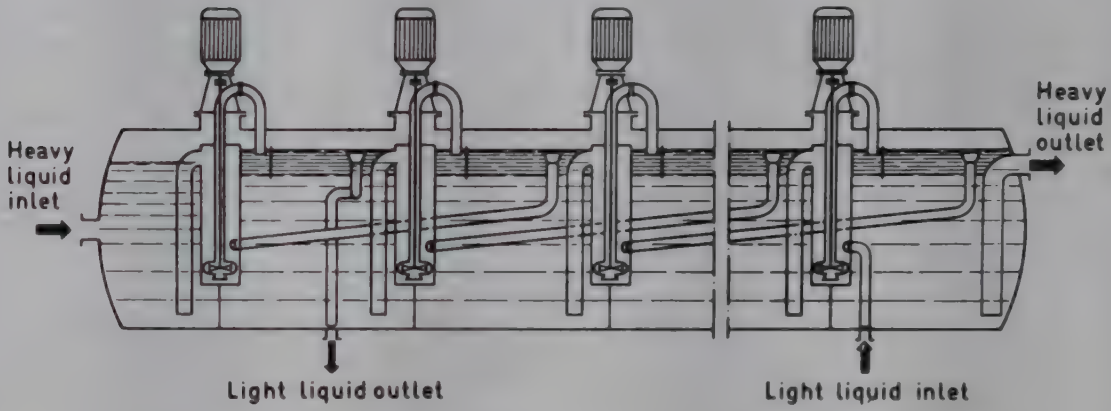
Heavy liquid inlet
Heavy liquid outlet
Light liquid outlet
Light liquid inlet

Fig. 2—Schematic arrangement of multi-stage extractor

The two streams of recovered solvent are combined and recycled to the extractor. The solvent-free weak liquor is discharged from the stripper and leaves the plant.

Until 1945 several plants operating by this method comprising 3 to 4 separate extraction- and separating-stages were built for dephenolization of effluents from l.t.c. and hydrogenation plants.

In 1949 a Phenosolvan plant was built and put on stream in 1950 for the l.t.c. plant at Offleben. This plant was the first to use a seven-stage extractor with fitted submerged pumps. Fig. 2 shows the arrangement of such multistage extractor.

It consists of a horizontal vessel comprising several compartments, each compartment being subdivided into a pumping chamber and a settling chamber. In the pumping chamber the effluent and solvent are intimately mixed, and the mixture is supplied to a settling chamber where the separation of effluent from lighter extract takes place due to the difference in their specific gravities. The effluent, being the heavy liquid, enters the extractor on the left and passes through a vertical pipe to the pumping chamber. Solvent, already partly loaded with phenols, enters the pumping chamber from the second settling chamber on the right, and the rotating pump impellers effect intermixing of the two liquids and their delivery to the first settling chamber by the principle of the mixer-settler process. The partly extracted effluent now enters the second pumping chamber in which it mixes with the phenolic solvent discharged from the third settling chamber. The procedure is continued from stage to stage until the last pumping chamber on the right has been reached where almost completely dephenolized effluent is mixed with fresh solvent.

From the first settling chamber the phenolic extract is discharged through an overflow funnel.

Fig. 3 shows a flow diagram of the Phenosolvan plant. The effluent, after precleaning in settling tanks and gravel filters, passes through scrubbing tower to the multistage extractor in which the phenols are extracted by Phenosolvan flowing in counter-current. Dephenolized effluent is stripped of dissolved Phenosolvan with steam in a stripper, the vapour being condensed in a subsequent column. The solvent-free weak liquor is discharged from the plant. The extract is treated in two distillation columns, one at atmospheric pressure and the other under vacuum, to recover the solvent;

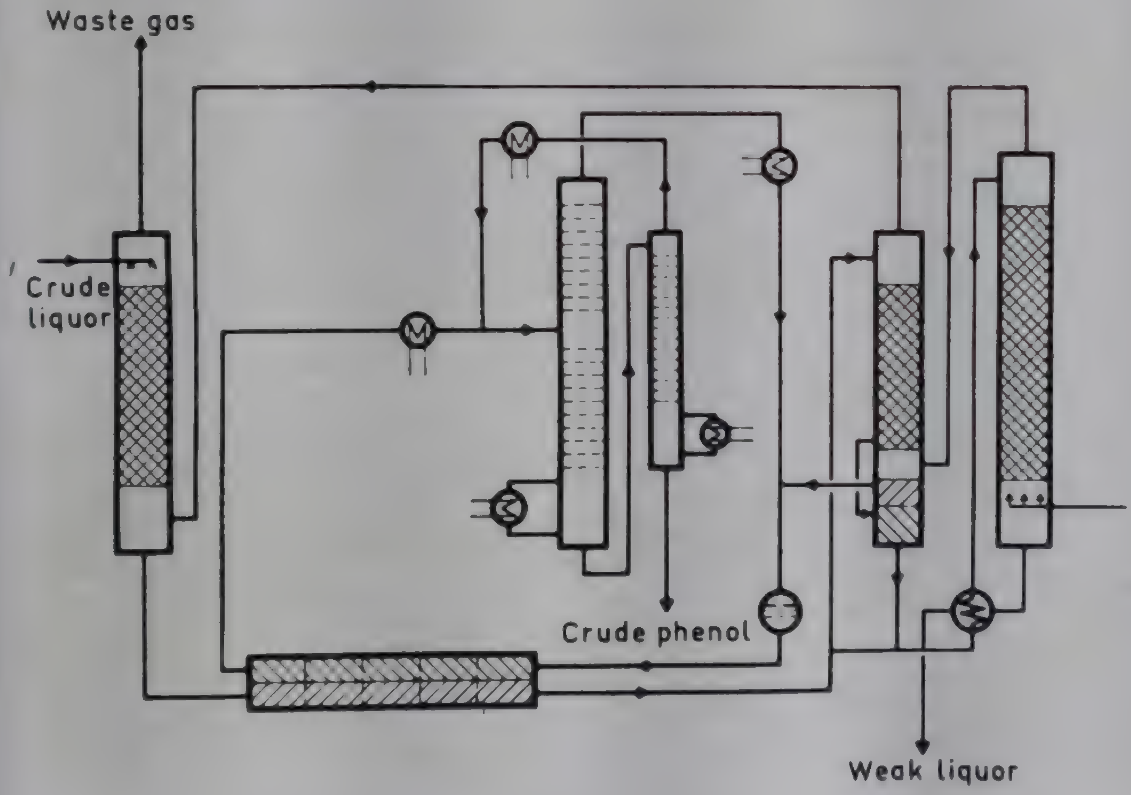

Fig. 3—Flow diagram of Phenosolvan plant

the crude phenol, which is recovered as distillation bottoms product is processed further to obtain pure products. The recovered solvent is recycled back to the extractor.

Fig. 4 shows the Offleben plant which was put on stream in 1950 and has a throughput of 23 cu. m./hr. Fig. 5 shows the same plant extended to a capacity of 32 cu. m./hr for the additional recovery of phenols from phenolic oil by pressure water extraction. This plant was the first to reduce phenols in the effluent to less than 10 mg./litre, corresponding to a yield of more than 99·9 per cent.

A large-scale test was conducted in this plant using methyl isobutyl ketone as a solvent, but the results did not show any special advantage for using this type of solvent as a substitute for butyl acetate. Although this ketone can be used as solvent, its solubility in water is twice as great (2 per cent) as that of butyl acetate resulting in difficulties during stripping of the dephenolized ketone-containing effluent for recovery of the solvent.

This Phenosolvan plant is made of ordinary steel, except for the vacuum column and the heaters which are of V4A stainless steel to protect them against attack by pyrocatechin present in brown coal phenols.

New Development in Phenosolvan Process. After the Phenosolvan process had proved successful for treatment of brown coal carbonization

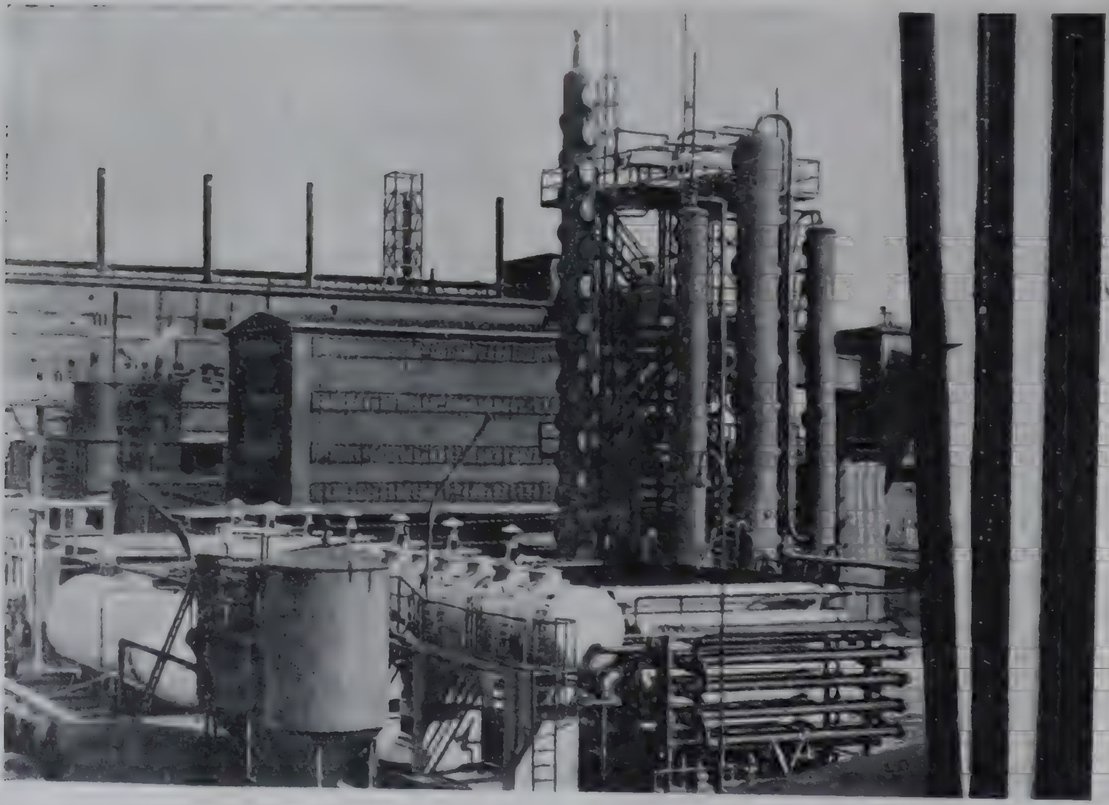

Fig. 4—Phenosolvan plant at Offleben

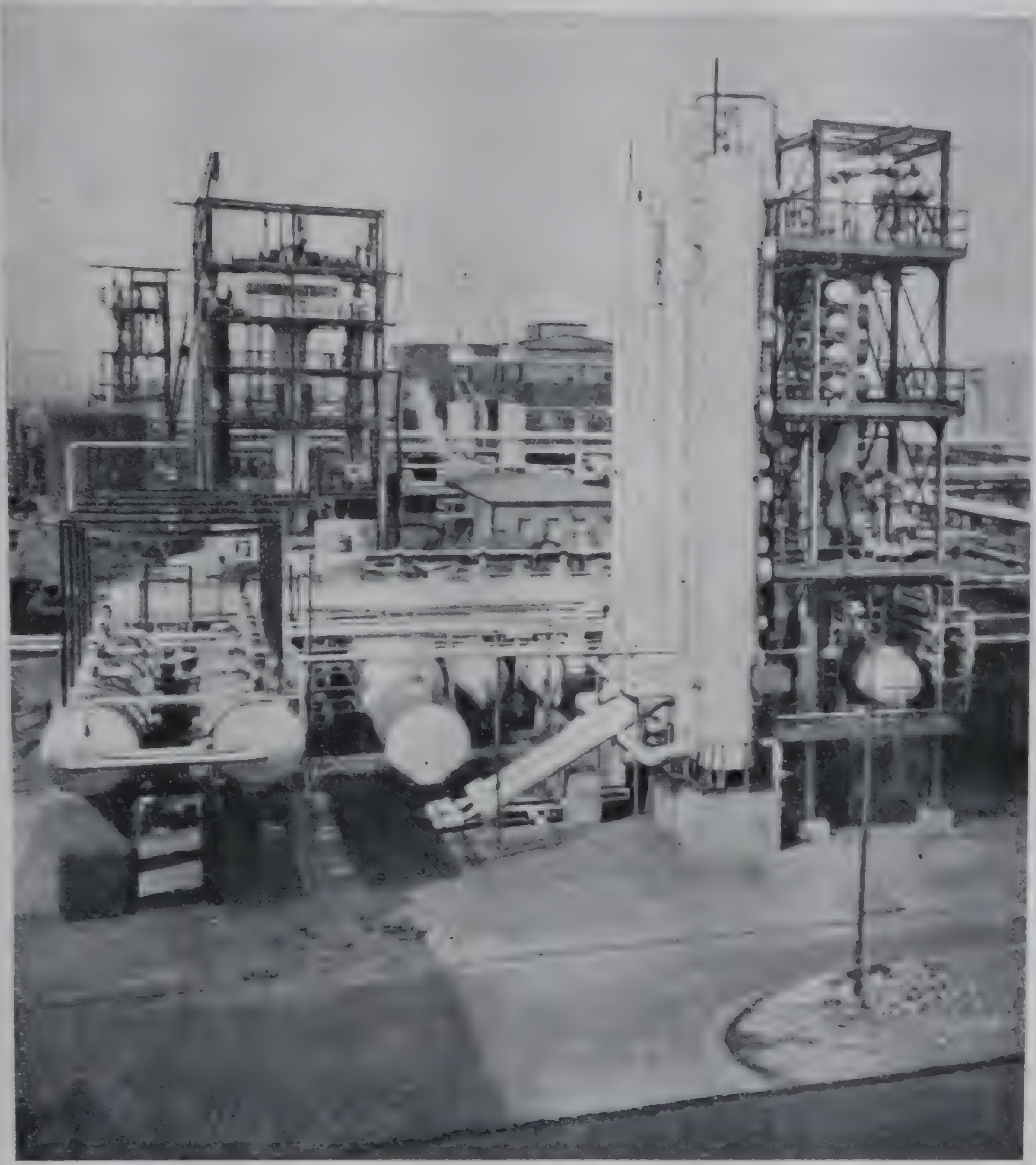

FIG. 5—EXTENDED PHENOSOLVAN PLANT AT OFFLEBEN

liquors of high phenol content (10-35 g./litre), it was the object of further development of the process to make it suitable also for dephenolization of coke-oven effluents containing low concentrations of phenols (1·5-3·0 g./litre). To achieve this, the process and equipment were improved and the overall cost reduced.

When using butyl acetate as solvent, losses may occur by saponification where the ammonia content is high in effluent, unless the ammonia is neutralized. Besides, the cost of butyl acetate is relatively high, viz. DM. 1·70 per kilogram. For these reasons isopropyl ether was selected as solvent in place of butyl acetate. The main characteristics of these two solvents are:

	Butyl acetate	Isopropyl ether
Boiling point, °C.	127	67
Distribution factor	45	22
Solubility in water, %	1	0·8
Price, DM./kg.	1·70	0·70

Apart from eliminating the possibility of saponification, other advantages of using isopropyl ether are:

1. Its boiling point is 60° lower, making solvent recovery by distillation easier. Low pressure steam will be sufficient and vacuum will not be required.
2. The difference in price of DM. 1 per kilogram means a saving of roughly DM. 50,000 per annum, for a large plant with an annual consumption of 50,000 kg. of solvent.

The disadvantage involved in the lower distribution factor can be offset by providing additional extraction stages or by increasing the quantity of circulating solvent.

The improvement in the equipment of Phenosolvan plant consists in replacing the horizontal cylindrical extractor by the box-type extractor. The advantage of this system is that the ratio of separating height and width can be varied, and that the extractor volume can be better utilized, resulting in lower cost. Fig. 6 shows a simplified flow diagram of box-type extractor.

Mixing pump arranged at the front end of the box delivers liquid mixture to the opposite end of the box so that separation of the two layers occurs across the complete length and width of the box, as indicated by arrows. Also, this extractor operates by the counter-current flow principle.

Fig. 7 shows a ten-stage box-type extractor in a commercial plant and Fig. 8 an overall view of a box-type extraction plant for 600 cu.m. of effluent per day.

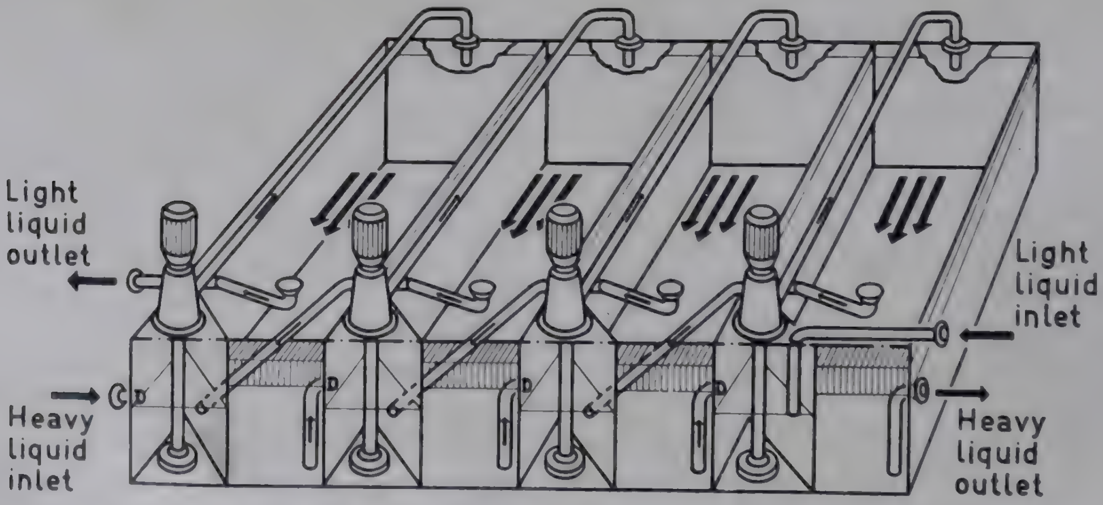

FIG. 6—SIMPLIFIED FLOW DIAGRAM OF MULTI-STAGE BOX-TYPE EXTRACTOR

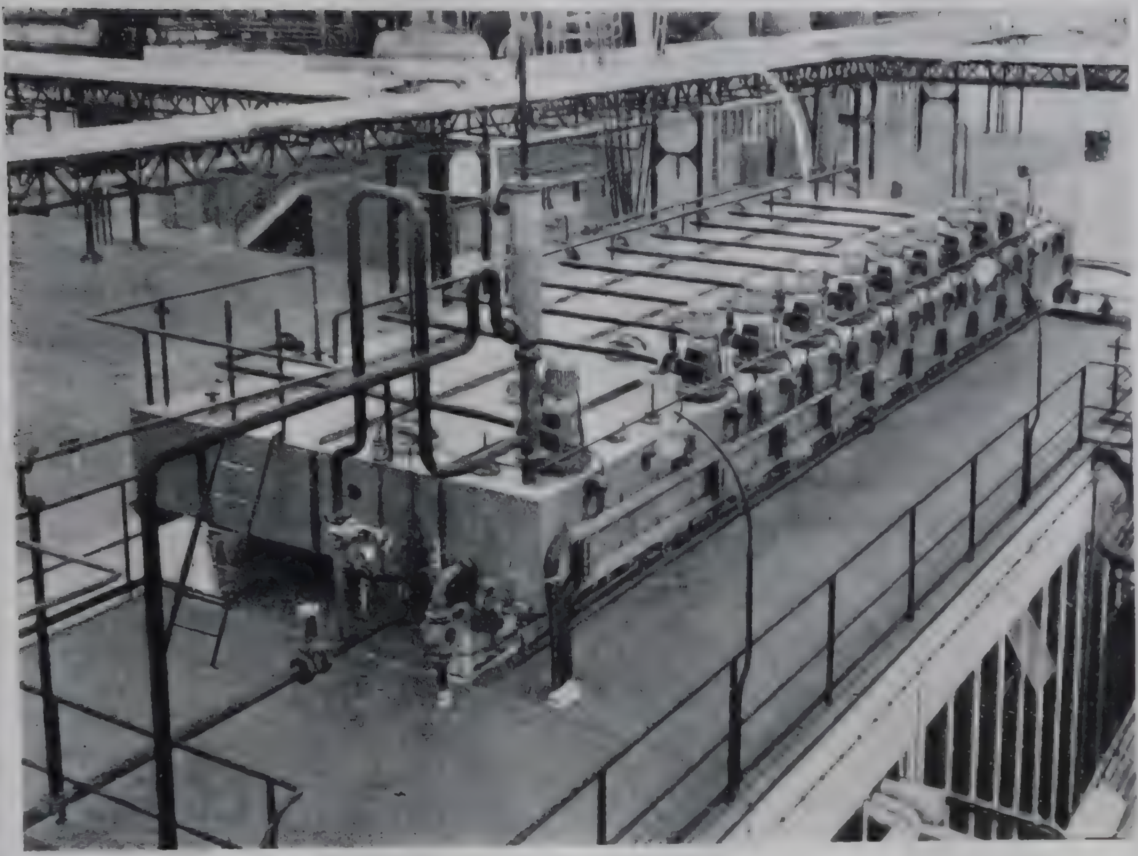

FIG. 7—HORIZONTAL TEN-STAGE BOX-TYPE EXTRACTOR

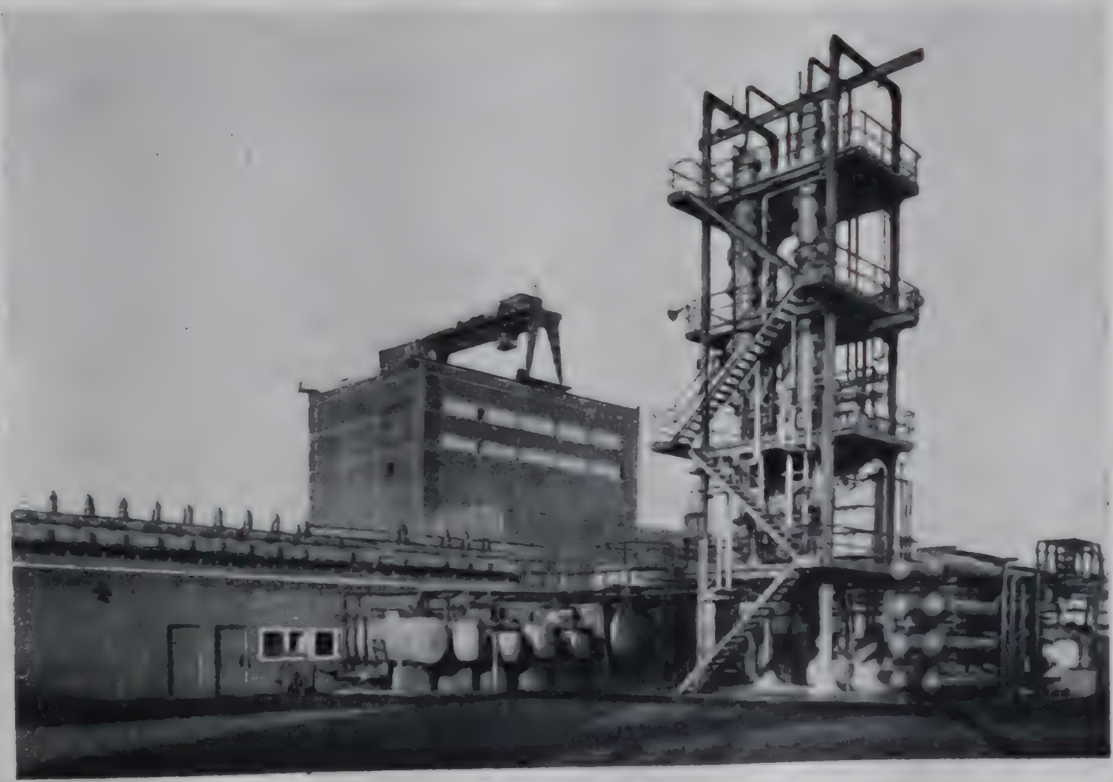

FIG. 8—OVERALL VIEW OF A BOX-TYPE EXTRACTION PLANT FOR 600 cu.m. EFFLUENT PER DAY

In connection with the substitution of isopropyl ether for butyl acetate for the purification of coke oven effluents, the following should be noted:

Solubility curves for the two solvents show that at the extraction temperature of about 35°C. a small quantity of solvent is dissolved in the effluent. For butyl acetate this amount is about 1 per cent, and for isopropyl ether about 0·8 per cent by weight. In Phenosolvan plants handling effluents from l.t.c. and pressure gasification plants, this solvent is recovered by steam stripping. In view of the steam requirements of 30-40 kg. per cubic metre of effluent this procedure is not commercially economical for Phenosolvan plants treating coke-oven effluents. Other methods had therefore to be found for solvent recovery. One of these methods is illustrated in Fig. 9

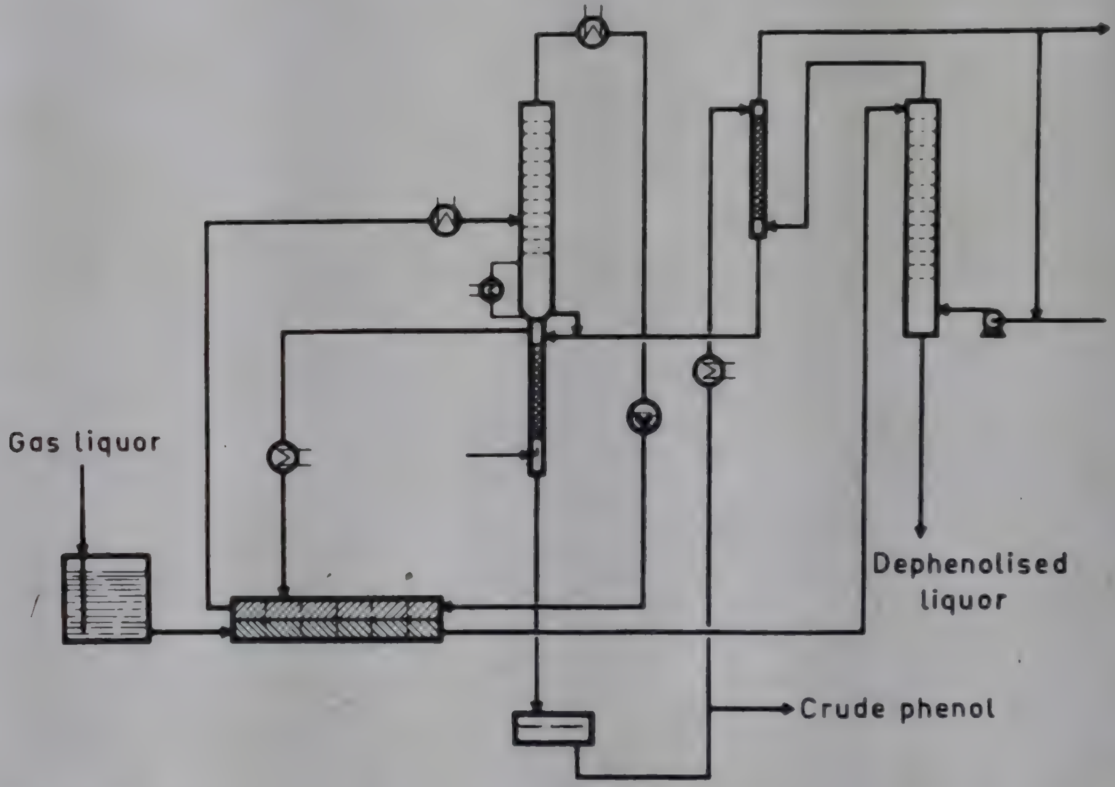

FIG. 9—SIMPLIFIED FLOW DIAGRAM OF PHENOSOLVAN PROCESS FOR THE DEPHENOLIZATION OF COKE-OVEN EFFLUENTS

After passing through the extractor the waste liquor is fed to a stripper in which benzol-free coke-oven gas or producer gas is blown from the bottom. The gas concentrated with solvent is washed in a wash tower with cooled crude phenol, after which it is returned to the stripper.

A small quantity of fresh gas is added to the cycle, and an appropriate amount of contaminated gas is discharged at a suitable point. The crude phenol required for the wash tower is taken from the crude phenol tank and is finally returned to distillation. As described already, the solvent is separated from the phenolic extract by distillation.

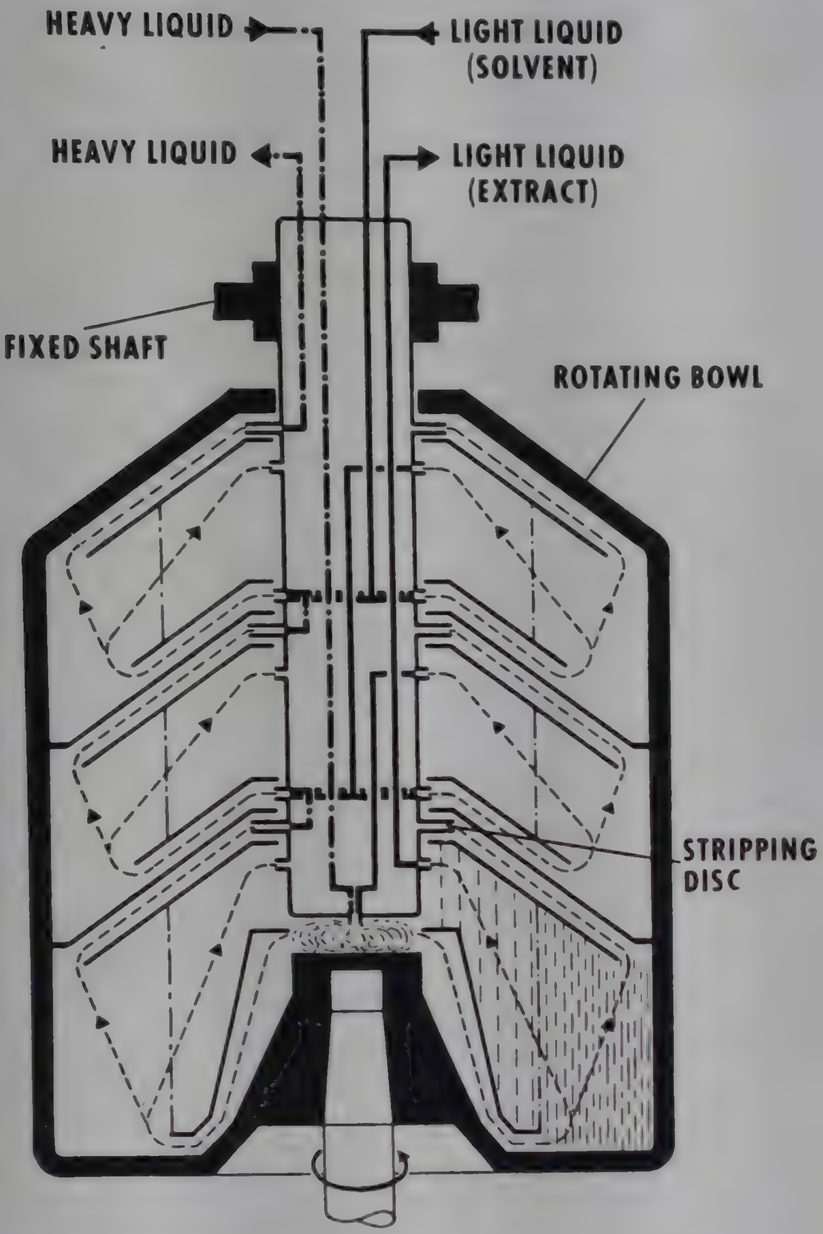
HEAVY LIQUID
LIGHT LIQUID (SOLVENT)
HEAVY LIQUID
LIGHT LIQUID (EXTRACT)
FIXED SHAFT
ROTATING BOWL
STRIPPING DISC

Fig. 10—Section through a two-stage bowl

Luwesta Extractors. Reference may be made to the Luwesta extractor (Fig. 10) which operates by the principle of mixing two liquids and their separation from each other and which furnishes favourable extraction efficiencies. Although these extractors are chiefly used in the chemical and pharmaceutical industry, they have also been used successfully for effluent purification, and in particular for the extraction of phenols from effluents.

NUMBER OF STAGES AND EFFICIENCY

From a chart published by Grob, the efficiency at a given number of stages or the number of stages necessary for any required yield can be determined. The charts were plotted on the basis of the Underwood equation for the graphical calculation of extraction phenomena.

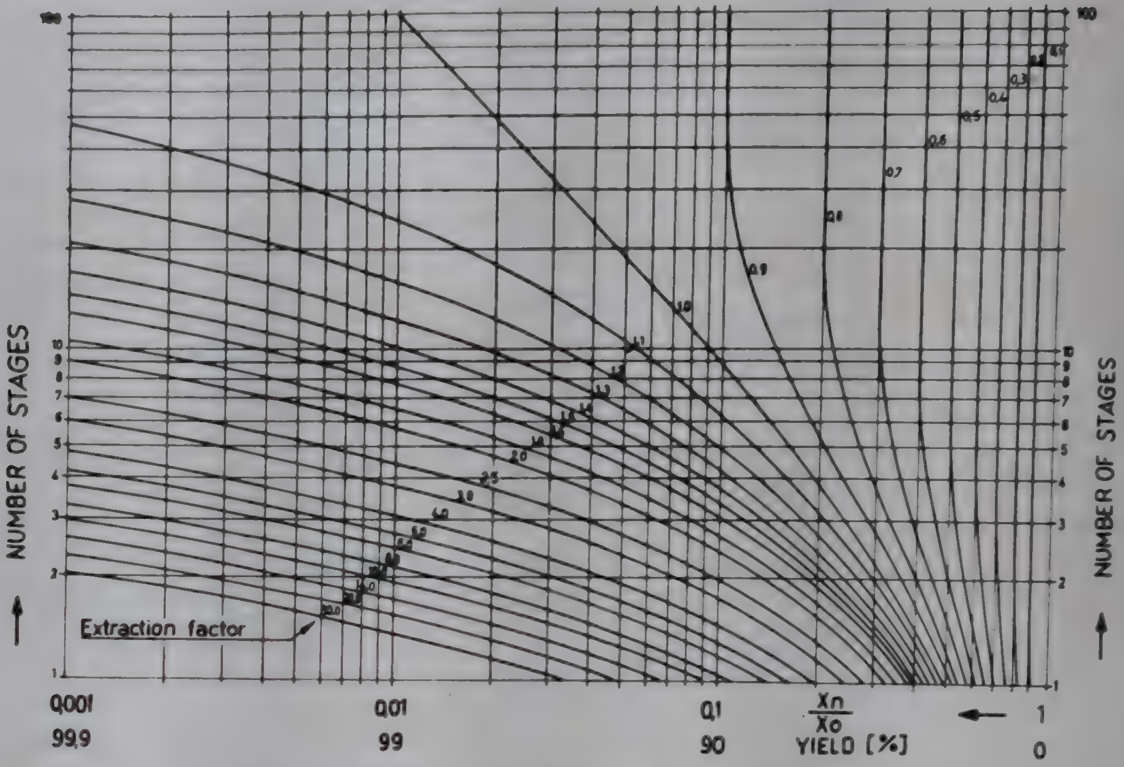

FIG. 11—COUNTER-CURRENT EXTRACTION: efficiency, no. of stages and extraction factor

The operating cost for the original Phenosolvan process with a daily throughput of 500 cu. m. of effluent amount to roughly DM. 3 per cubic metre of effluent, including capital charges.

When handling carbonization liquor, this plant furnishes roughly 12 kg. of crude phenol per cubic metre of effluent which can be priced at DM. 0·40 per kilogram.

When using isopropyl ether as solvent and box-type extractors, the operating cost is roughly DM. 1·40 per cubic metre of effluent. The operating cost of this improved Phenosolvan process is sufficiently low so as to be economic for treatment of coke oven effluents also, since the recovered crude phenol can be priced at DM. 0·50 per kilogram.

During the past few years, several Phenosolvan plants for the dephenolization of coke-oven effluents were installed, proving their technical and economical feasibility in this field also.

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New Developments in the Dephenolization of Coal Tar Oils and Ammoniacal Liquors and Recovery of Pure Phenolic Compounds

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The different methods of dephenolization of tar oils and ammoniacal liquor, viz. extraction with caustic soda, Pott-Hilgenstock process and Phenosolvan processes are briefly described and their essential principles pointed out. The various properties required of the solvents to be used for extraction of phenols from aqueous solutions are given. Work carried out by Firma Carl Still of finding suitable solvents for the purpose is briefly indicated. A detailed description is given of a tar dephenolization plant using sodium phenolate solution as the absorption media and iso-octadecanol as the solvent. A pilot plant for dephenolization of ammoniacal liquor is also described.

During low temperature carbonization (l.t.c.) of lignite and bituminous coal and high temperature carbonization of bituminous coal, tars and waste water containing phenols are obtained.

In the case of waste waters, phenol can be directly extracted after purification through filtration and subsequent washing, for example, with benzol. But in the case of tar, prior distillation is necessary, to enrich the phenols in definite fractions which can be subsequently extracted.

For refining of tar, several modern methods are available. Among these are the continuous distillation plants for high temperature tar constructed by Firma Carl Still in Sterkrade and Salzgitter in Germany and in Linz in Austria. Another plant of this type is being constructed at Durgapur in India.

Due to high phenol content of the low temperature (l.t.) lignite tar, refining of this tar has a special significance in connection with phenol recovery.

The plant constructed by Firma Still in Espenheim near Leipzig for treating about 700 tons of l.t. tar per day, the capacity of which could be extended to 1000 tons per day is particularly mentioned here. This plant has already been referred to in literature.

The flow and working diagram of this plant can be seen from the Figs. 1 and 2.

The products obtained are, carbolic acid, cresols, xylenols, gasoline, diesel oil, fuel oil, hard and soft paraffins, road tar, carbon for electrodes, benzol, tar and gas from coking of hard pitch.

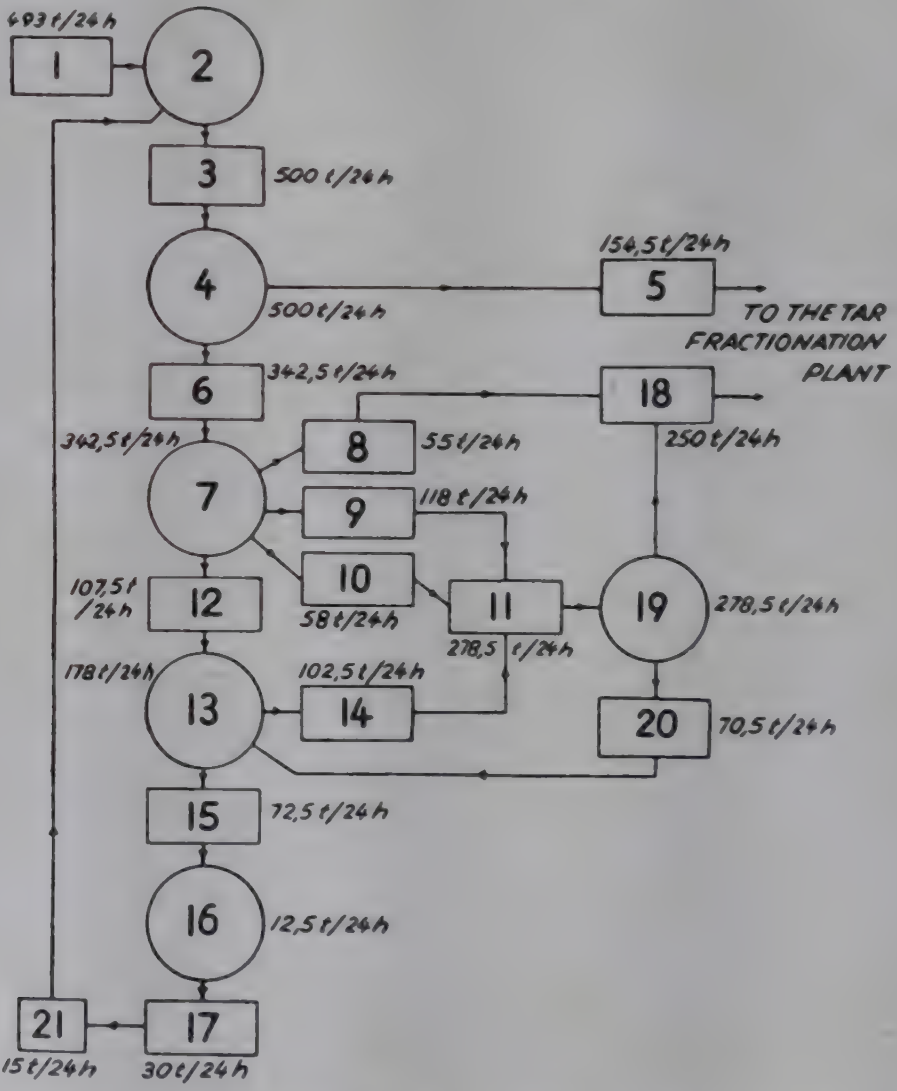

493 t/24 h
1
2
3
500 t/24 h
154,5 t/24 h
4
500 t/24 h
5
TO THE TAR FRACTIONATION PLANT
6
342,5 t/24 h
18
342,5 t/24 h
8
55 t/24 h
250 t/24 h
7
9
118 t/24 h
107,5 t /24 h
12
10
58 t/24 h
11
278,5 t/24 h
19
278,5 t/24 h
178 t/24 h
13
102,5 t/24 h
14
20
70,5 t/24 h
15
72,5 t/24 h
16
12,5 t/24 h
21
15 t/24 h
17
30 t/24 h

FIG. 1—SCHEME OF THE TAR PROCESSING PLANT: (1) Crude tar, (2) Tar centrifuge, (3) Pure tar, (4) Atmospheric distillation, (5) Heavy oil, (6) Residue, (7) Vacuum distillation, (8, 9, 10, 11 and 14) Paraffin mass, (12, 20) Soft pitch, (13) Inert gas distillation, (15) Hard pitch, (16) Pitch coke-ovens, (17) Electrode coke, (18) Redistillate, (19) Redistillation, (20) Coke-oven tar

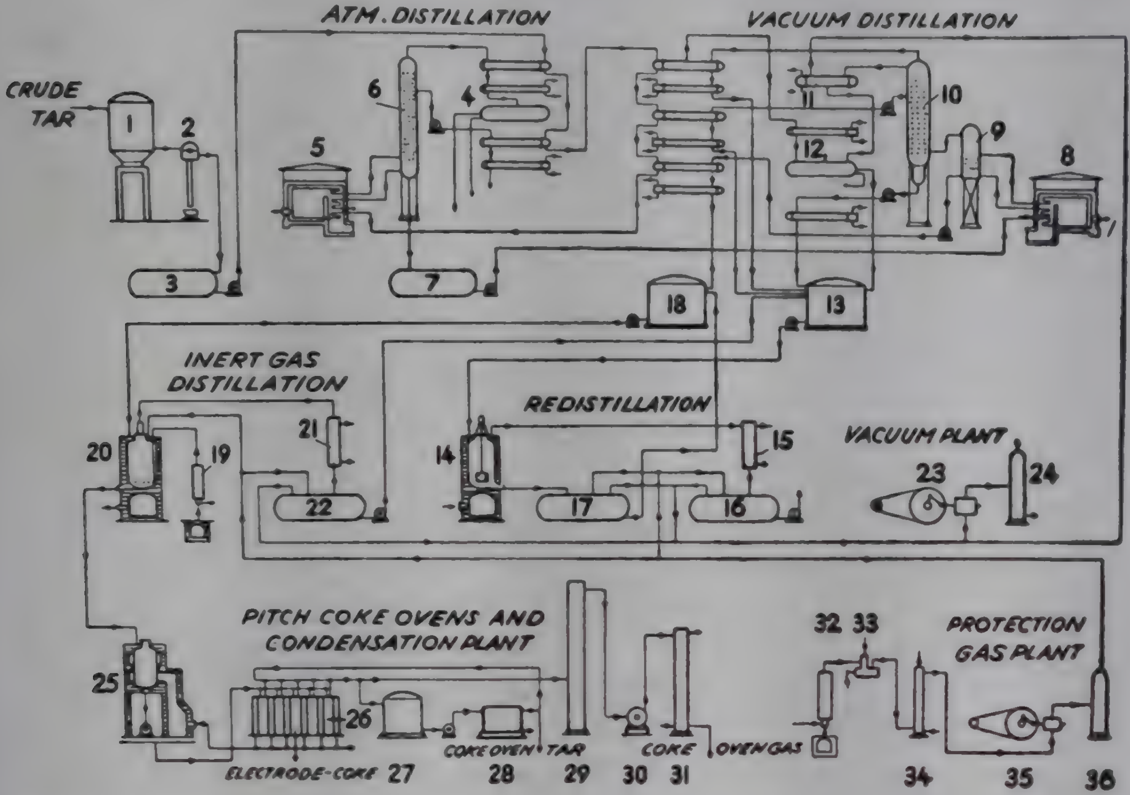

ATM. DISTILLATION
VACUUM DISTILLATION
CRUDE TAR
1
2
3
4
5
6
7
8
9
10
11
12
13
18
INERT GAS DISTILLATION
REDISTILLATION
VACUUM PLANT
14
15
16
17
19
20
21
22
23
24
PITCH COKE OVENS AND CONDENSATION PLANT
PROTECTION GAS PLANT
25
26
COKE OVEN
TAR
COKE
OVEN GAS
ELECTRODE-COKE
27
28
29
30
31
32
33
34
35
36

FIG. 2—SCHEME OF THE TAR PROCESSING PLANT: (1) High level tank, (2) Tar centrifuge, (3) Pure tar, (4) Separator, (5,8) Still, (6, 10) Main column, (7) Residue, (9) Pre-evaporator, (11) Condensator, (12) Separator, (13) Paraffin mass, (14, 20) Distillation still, (15, 21, 28, 34) Cooler, (16) Redistillate, (17, 18) Soft pitch, (19) Protection gas producer, (22) Inert gas distillate, (23) Vacuum pump, (24) Exhaust vessel, (25) Cooling still, (26) Pitch ovens, (27) Flushing tar tank, (29) Direct cooler, (30) Gas exhauster, (31) Indirect cooler, (32) Combustion chamber, (33) Water container, (35) Protection gas compressor, (36) Pressure vessel

Phenols present in tar oils can be removed by different methods, e.g. physically, by methyl alcohol—water mixture, or chemically, by means of soda solution under pressure and at high temperature. By far the most commonly used process is, however, the direct reaction with sodium hydroxide, to give sodium phenolate as in the case of soda process, without application of pressure and temperature. Phenols are acidic in character and, therefore, can form salts with bases. In most cases, phenol from sodium phenolate can be freed by passing carbon dioxide or gases containing carbon dioxide. From soda or sodium bicarbonate solution, phenols can be mechanically separated and further processed. The carbonate solution containing small amounts of phenols and bases cannot be profitably added to the waste water. The carbonate should be regenerated with quicklime. Sodium hydroxide is recovered and returned to the process. By the double decomposition calcium carbonate is formed, which can be again burned to quicklime. But the product is very fine, granular and hydrophyllic and, therefore, the recovery is rather expensive. Quicklime obtained by burning freshly ground limestone is therefore used in practice. The used-up calcium carbonate obtained as side product is dumped out.

In the classical Pott-Hilgenstock process for the dephenolization of ammoniacal liquor, phenol is extracted with benzol which is subsequently recovered with caustic soda. The phenolate should then be decomposed with carbon dioxide for the recovery of phenol. The carbonate solution from this should also be causticized with quicklime. This process also produces heaps of used-up calcium carbonate. This method is chemically simple and reliable, although it is always coupled with the formation of lime heaps. Attempts were therefore made to find other methods of removing phenols from waste liquor and oil. Primarily it was a question of finding out other new extraction media, which do not require such type of regeneration.

By treating the liquor with low boiling oxygen-containing organic substances such as aliphatic alcohols, ethers, esters and ketones, dephenolization is possible. These substances have got a higher solubilizing capacity for phenol than benzol or, any other definite aromatic fractions from coal distillation used in Pott-Hilgenstock process. Due to the great differences in their boiling points the separation of phenols from extraction media is relatively simple. The Phenosolvan process works on this principle.

Non-aqueous, phenol-containing oil mixtures cannot be directly extracted with organic solvents, since they are miscible with oil in all proportions. However, organic water-soluble substances, e.g. methyl alcohol can be used. By admixing with water extraction media which selectively take up phenols, bases are obtained. The neutral components in the tar oils dissolve only in small proportions. The treatment of such extracts and the recovery of the organic components of the solvents are, however, rather complex processes.

The solubility of phenol in water offers another possibility for the extraction of phenols from oils. It is rather low at low temperature and rises steeply with increase of temperature. An effective extraction can be obtained only above 100°C., under pressure requiring costly apparatus. The higher absorbing capacity of water for phenol at low temperature can, however, be increased when certain substances are dissolved in it, e.g. pure salts, mostly the salts of strong bases and weak acids. The salts such as sodium phosphate, sodium acetate, and sodium salts of some aliphatic and aromatic acids may be mentioned here. The phenols themselves are weak acids, and as such, are capable of combining with bases to form salt-like compounds. Such a salt formation occurs in the sodium phenolate solution. It is known for a long time that the aqueous sodium phenolate solution can physically dissolve phenol up to 250 per cent, far above the stoichiometric proportions. It is spoken of as that the phenolate gets supersaturated. As the supersaturated phenols are physically dissolved, it is possible to extract them with organic solvents of high solvent capacity, so that only the chemically combined phenols in the sodium phenolate solution are left behind. Therefore, a solvent with low solubility in water and a boiling point different from that of the phenols is chosen, so that the phenols can be finally separated and recovered by distillation. The extraction of supersaturated phenolate solution is possible by means of the same organic solvents as are used for the dephenolization of liquor. This method is used in the so-called 'Phenoraffinverfahren' process.

In many cases it is convenient to work with phenolate solution because it is formed automatically when phenol-containing oils are extracted with sodium hydroxide. It is, however, better to work with less than 250 per cent supersaturation of the chemically combined phenol fraction because the supersaturated phenolate solution is also a solvent for the neutral oils.

Before the phenols are extracted from the salt solution, the dissolved neutral oils can be separated by washing with hydrocarbons having a low solubility for the phenols. Naphthalene and its homologues chiefly interfere in this process. At this stage the further purification of the phenolate solution depends on the purity required of the phenols being recovered.

Use of oxygen-containing organic solvents, the boiling points of which lie far below than those of phenols is well known. Due to their high dissolving capacity they are promising; they are, however, not wholly insoluble in water and for the economic extraction they should be recovered from the aqueous solution or waste water. Di-isopropyl-ether (b.p. 68°C.) has a solubility of 0·2 g. in 100 cc. water at 20°C. Other oxygen-containing organic substances which have nearly the same boiling points give the same yields. Actually, in the water-soluble extracting media more of the fractions dissolve because the contents of the ammoniacal liquor and the phenolate solutions serve as emulsifiers to some extent.

If a high boiling substance is used, then there is no danger of solubility in water. Although these high-boiling solvents have somewhat low dissolving capacity for phenols, they are satisfactory enough if they fulfil the following important properties:

(1) The dissolving capacity for the phenols should be so high that sufficient dephenolization is secured. (2) They should have high boiling points so that the phenols can be separated from them by distillation. (3) High insolubility in water should be safeguarded. (4) Tars and neutral oils should be soluble only in small proportions. (5) They should not have any polymerising tendency. (6) They should be thermally and chemically stable.

Till now tricresylphosphate with a boiling point of 280-285°C /10 mm. mercury has been the only high boiling solvent used for phenol extraction. In this process, the tars and asphalts must often be separated during the process and the solvent is not quite free from polymerizing properties. The polymerizing property of phosphoric acid itself is well known. Two of the important requirements, are thus not fulfilled.

For the past few years high-boiling alcohols, ethers, and esters, chiefly, with branched carbon chains in the molecules have been examined by the Firma Carl Still, and the substances have been found to be suitable for the dephenolization of tar oils and ammoniacal liquor and fulfil the above-mentioned requirements.

Work has been chiefly concentrated on the use of high-boiling alcohols, which have the highest solvent capacity for phenols. Such substances are now-a-days obtainable in the market. They can be prepared for example, by Roelen's Aldehyde synthesis, where di-isobutylene, tri-isobutylene, tripropylene, carbon monoxide and hydrogen serve as the starting substances with cobalt salt as catalyst.

From the work carried out by the Firma Carl Still, it has been established that all alcohols, ethers and esters having the same structure, irrespective of the way they have been prepared, are suitable for the dephenolization. At present the oxosynthesis or the formylization, so-called Roelen's Aldehyde synthesis is the only practical method for their preparation.

The phenols present in ammoniacal liquor and tar oils boil generally up to 225°C. at atmospheric pressure. Iso-octadecanol prepared from di-isobutylene has a b.p. of about 310°C. There exists, therefore, a marked difference in the boiling points of the phenols and their solvents.

Laboratory experiments with ammoniacal liquors, have exhibited favourable distribution coefficients of 8-16 as compared to the coefficients of 2-2·5 for the aromatics used in Pott-Hilgenstock process. The distribution coefficient of tricresylphosphate reported in literature, is still better, about 60.

In later experiments and in large-scale continuous processes it has been found further that tar compounds and neutral bodies are not very soluble at ordinary temperature. By cooling to 25-30°C. they are settled to a large extent in the separator and can be removed before the solvent returns to the dephenolization cycle.

The polymerizing property is absent. Even on the basis of chemical nature of the solvents, this could hardly be explained.

The actual physical solubility of these solvents in water is so low that one can forego a recovery from the aqueous phase, without much financial loss. In the treatment of usual waste liquor and tar oils no emulsion is formed. From the preliminary experiments, conducted with a charge of 100 litres/hr, it has been found that further experiments with this group of solvents, are profitable.

The important results of these preliminary experiments are: (1) The phenols obtained are by far very pure. Those obtained from waste liquor have a purity of 80-90 per cent and from tar oils 99·8 per cent. In both the cases there are some impurities of small amounts of bases, some neutral components and water. (2) The solvent losses are low. (3) Energy and equipment costs will not be exhorbitantly high.

On the basis of the experimental data, large-scale plants have been set up from which useful knowledge has been gained.

The working principle of such a tar dephenolization plant is described in Fig. 3.

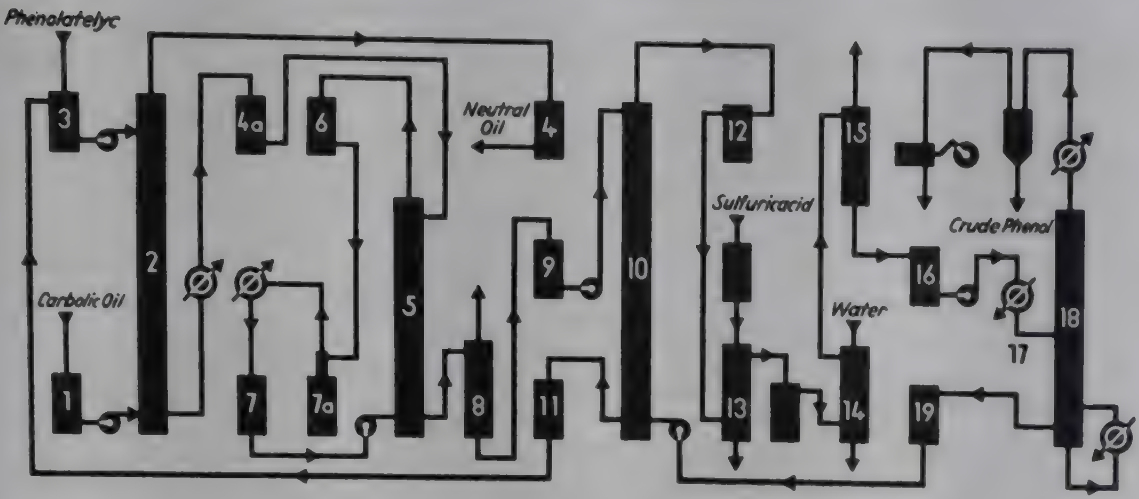


Fig. 3—Flow diagram of dephenolization plant: (1) Storage vessel for carbolic oil, (2) Extractor, (3) Phenolate lye storage, (4) Separator vessel, (4a) Separator, (5) Hydrocarbon column, (6) Water separator, (7, 11, 19) Container, (8) Steam flasher, (7a) Distillation, (9, 12, 16) Intermediate container, (10) Extractor, (13) Sulfuric acid scrubber, (14) Neutraliser, (15) Dehydration column, (17) Heater, (18) Rectification column

The preheated carbolic oil at a temperature of 60-70°C. from the storage tank (1) enters the extraction system (2) at the bottom. Simultaneously sodium phenolate solution containing 10 per cent sodium hydroxide and equivalent amount of phenol from the storage tank (3) enters the top of the extraction system (2). The dephenolized carbolic oil flows into the separator tank (4). Some of the phenolate solution which is carried along, is stripped off and the remaining oil leaves the plant. Now the phenolate solution containing phenol much above the stoichiometric proportions flows out from the bottom of the extraction system. The carbolic oil carried along is stripped off in the separator (4a) and the phenolate solution enters the top of the hydrocarbon column (5). Here the dissolved neutral oil fraction with the excess phenol is washed with the hydrocarbons in counter-current system at a temperature of 50-60°C., and is collected in the upper portion of a reserve tank (not shown here). From here it is conducted into the distillation column (7a) through the water separator tank (6), in amounts according to the requirements of the process. From there it returns to the process over the top of the column and receiver (7). The phenolate solution washed with hydrocarbons, collects in the column (5) and from there it is passed into the top of the steam-clarifying column (8), where the dissolved hydrocarbons are stripped off by steam in counter-current system. The condensation products consist of water and hydrocarbons with small quantities of phenols. Their further treatment follows by mixing them with the initial charges. The condensed water is utilized for producing steam for steam clarifying column and thus the phenols in this condensed water are returned to the cycle. Here it is equally good to set up a water dephenolization plant.

The supersaturated phenolate solution with phenol is now pumped into the extraction system (10) through the intermediate tank (9) and is extracted with the new solvent at a temperature of about 70°C in counter-current principle. The phenolate solution containing alkali and phenols in stoichiometric proportions leaves the extraction system at the bottom and enters the tank (11) where the remaining solvent separates and is returned to the process.

The extracted phenols dissolved in the solvent collect above in the extraction system (10). Then it is drawn off into the intermediate tank (12) in which the residual quantities of water separate out. Then it is successively passed into the sulphuric acid washer (13) to remove the bases and then into the neutralization washer (14). It then flows into the dehydration column (15), where the little quantities of water are removed from the top. The phenol-containing solvent is conducted into rectification column (18) via the intermediate tank (16) and heater (17). The rectification column provided with the heater is kept under reduced pressure. The solvent freed from phenols collects in the receiver (19) from where it again returns to the extraction process.

The solvent iso-octadecanol used here, has proved to be very stable. The loss of solvent is low. The loss due to pumps can be extensively avoided by taking proper steps. The iso-octadecanol fraction remaining in the phenolate solution in the cycle amounts to a maximum of about 2 gram per kilogram of phenol recovered. A portion of it can be again recovered.

A pilot plant for the dephenolization of the ammoniacal liquors with a capacity of 1·2 to 2 cu.m. water per hour has been set up to try new solvents. The working principle of this plant is explained in Fig. 4.

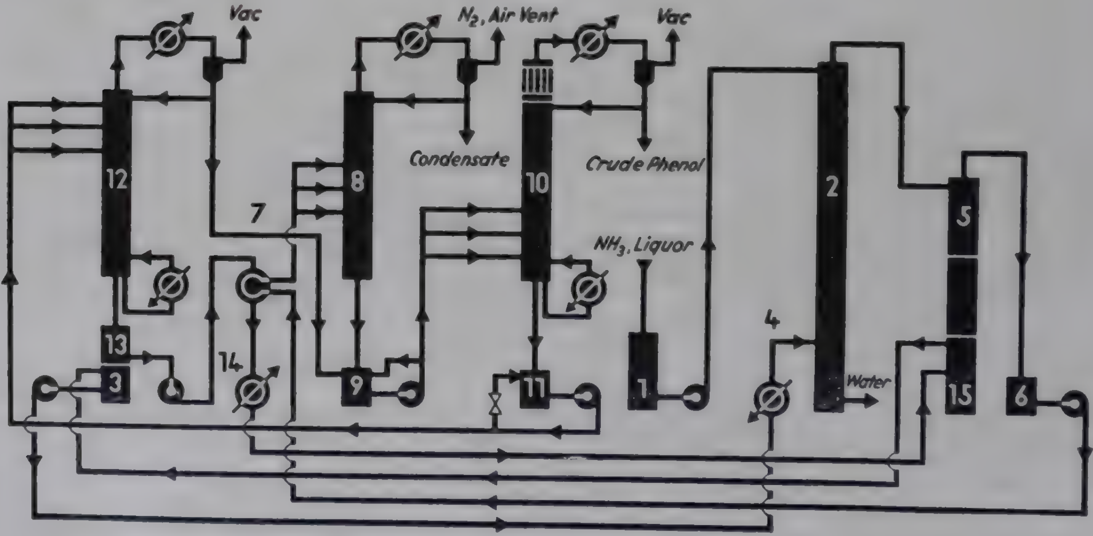
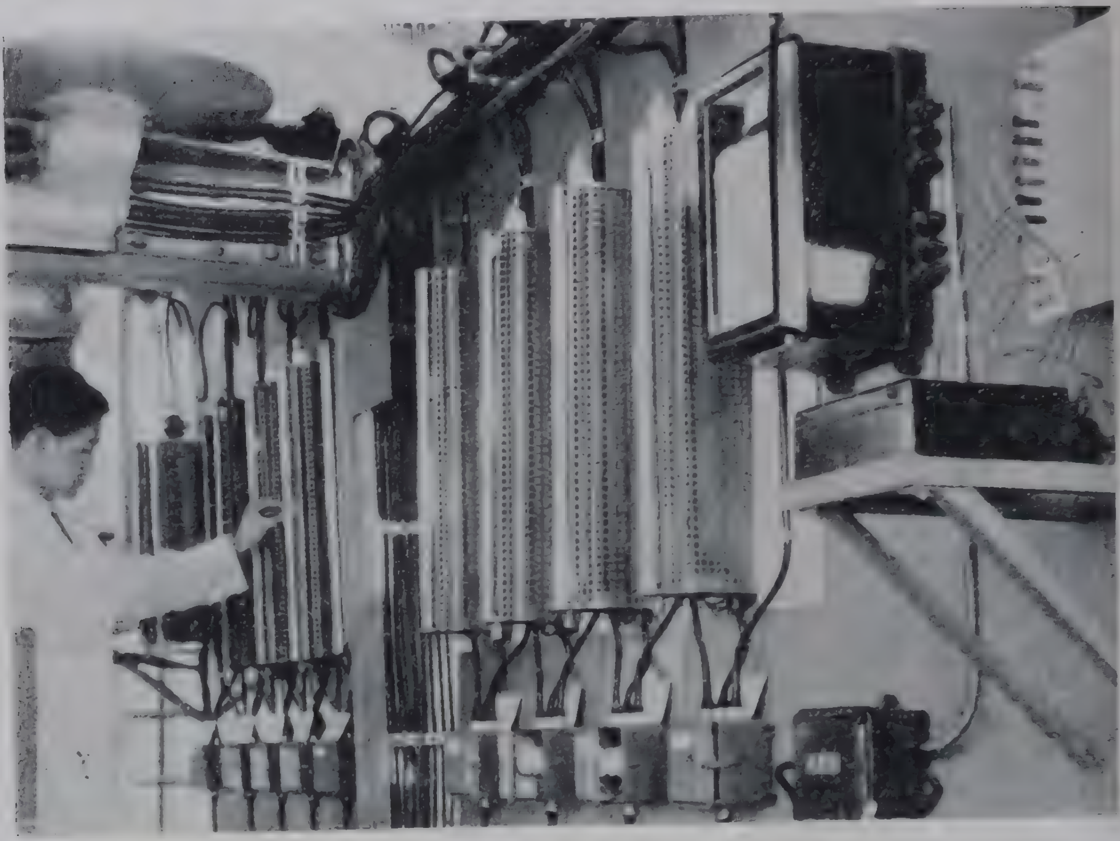
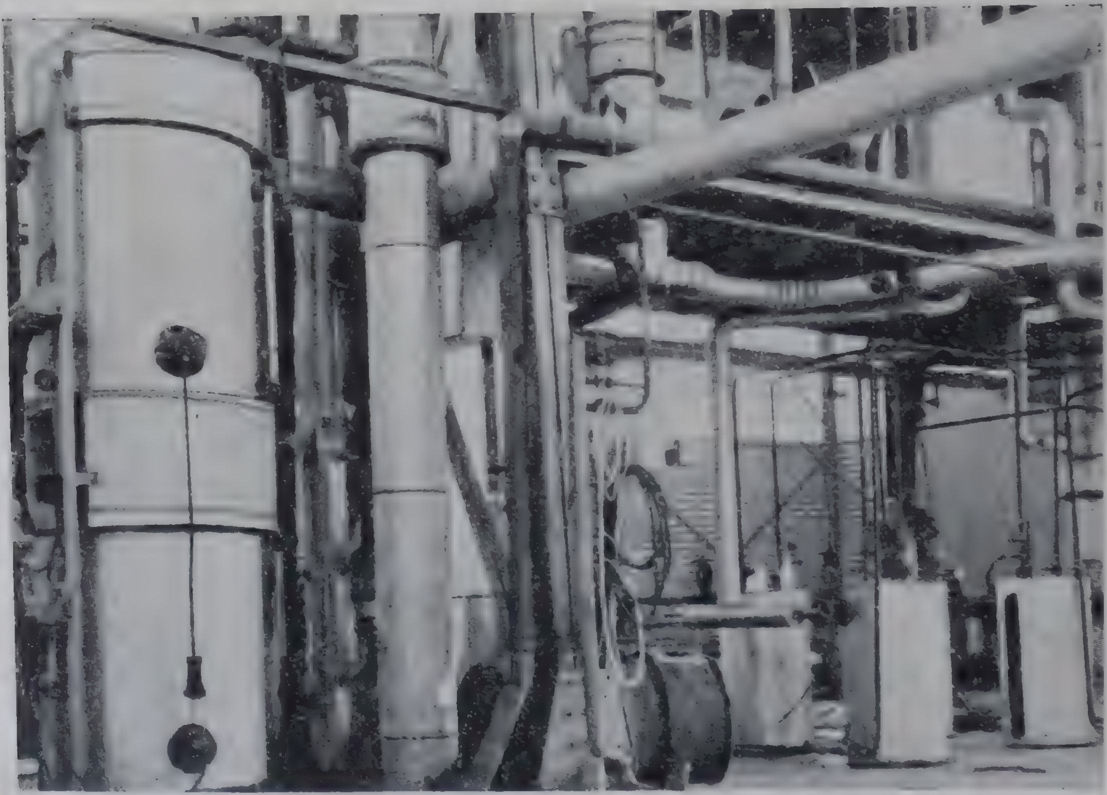


FIG. 4—FLOW SHEET OF PILOT PLANT FOR DEPHENOLIZATION OF AMMONIACAL LIQUORS: (1) Storage tank, (2) Extractor column, (3) Solvent collector tank, (4) Preheater, (5) Solvent separator, (6) Charge tank, (7) Heat exchanger, (8) Dehydration column, (9, 11) Tank, (10) Rectification column, (12) Stripping column, (13) Solvent tank, (14) Cooler, (15) Separating tank

FIGS. 5 AND 6—DIFFERENT VIEWS OF THE PILOT PLANT FOR DEPHENOLIZATION OF TAR





Figs. 7 and 8—Different views of the pilot plant for dephenolization of tar

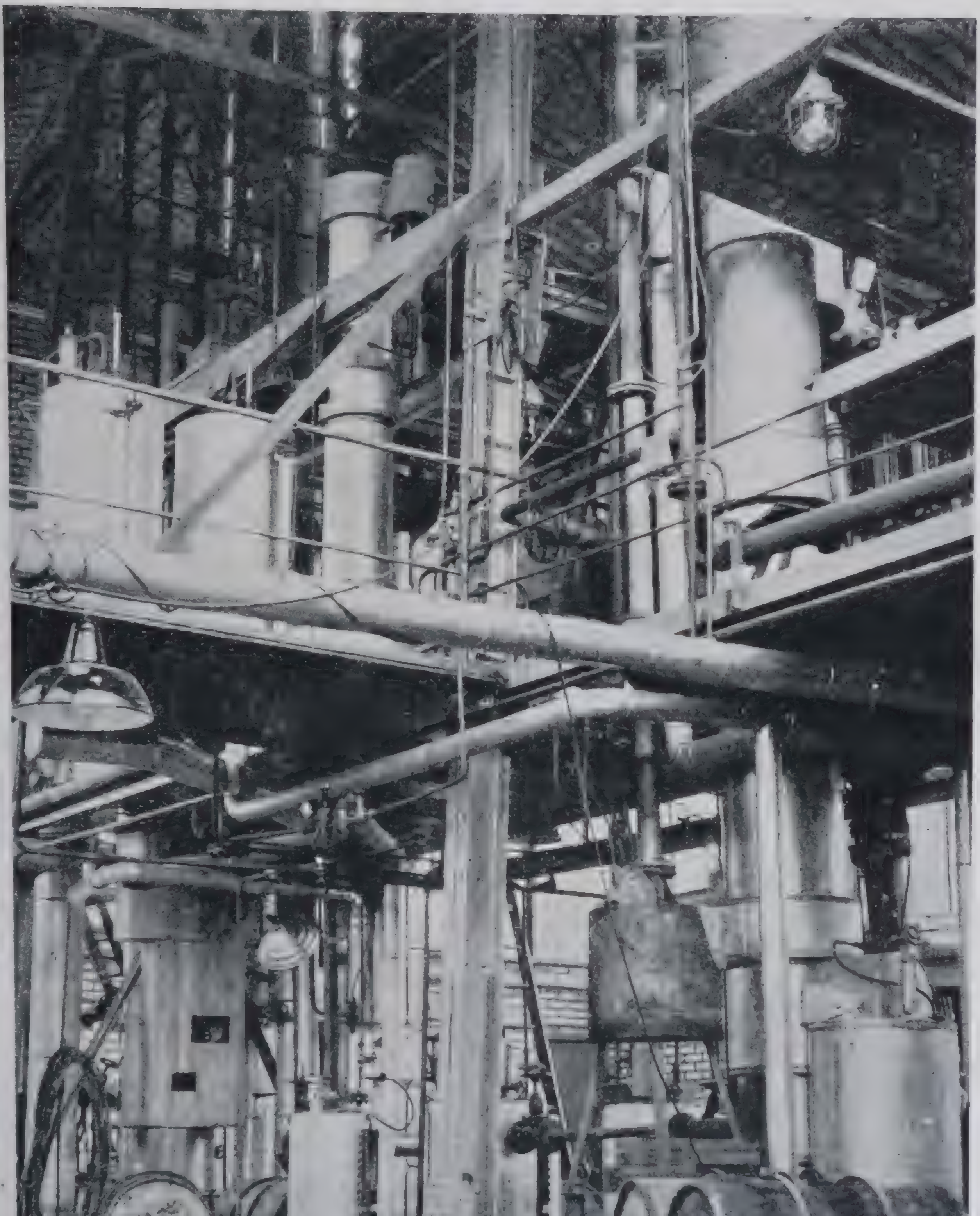


FIG. 9—ANOTHER VIEW OF THE PILOT PLANT FOR DEPHENOLIZATION OF TAR

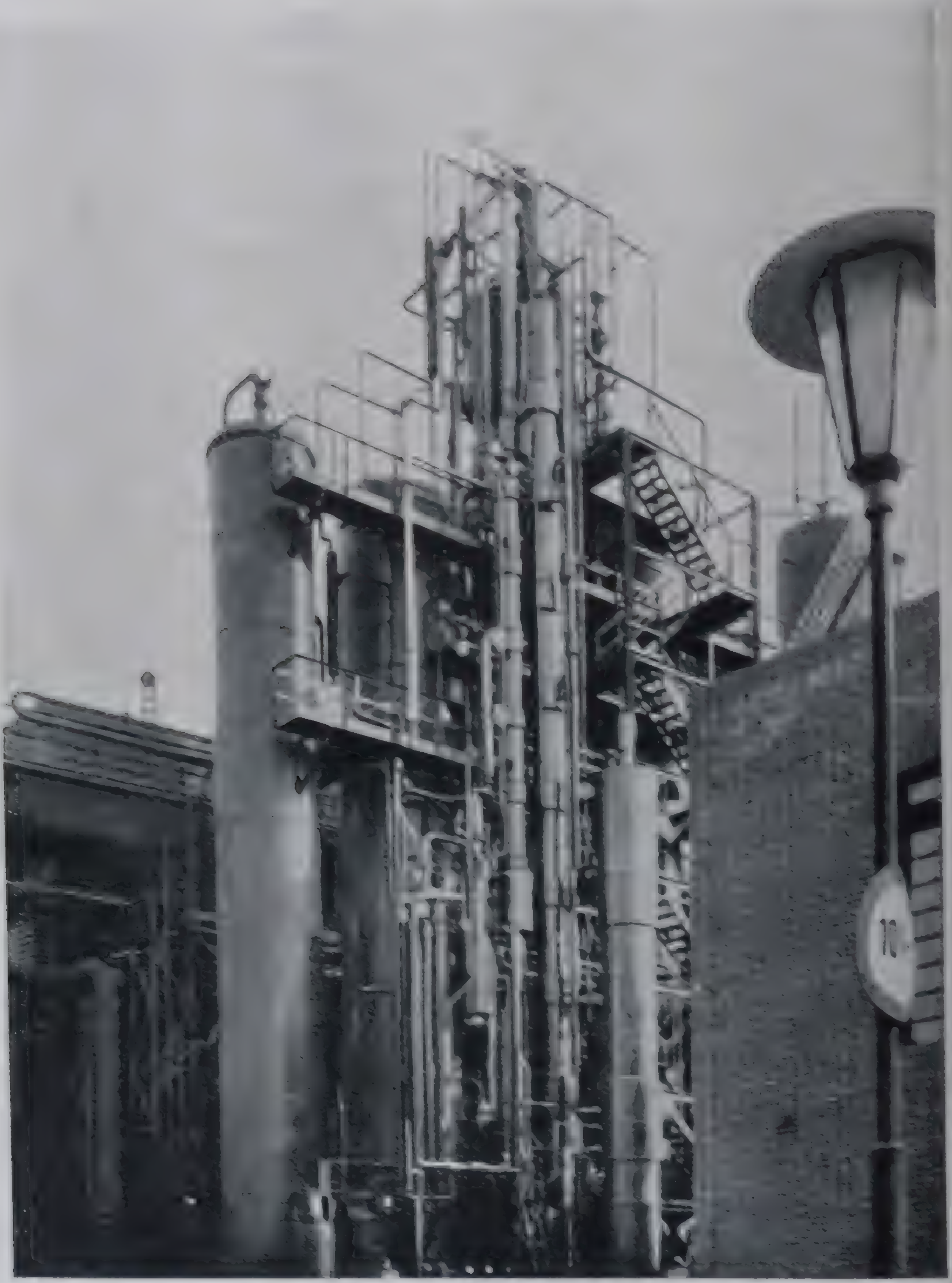


FIG. 10—A VIEW OF THE PILOT PLANT FOR DEPHENOLIZATION OF LIQUORS

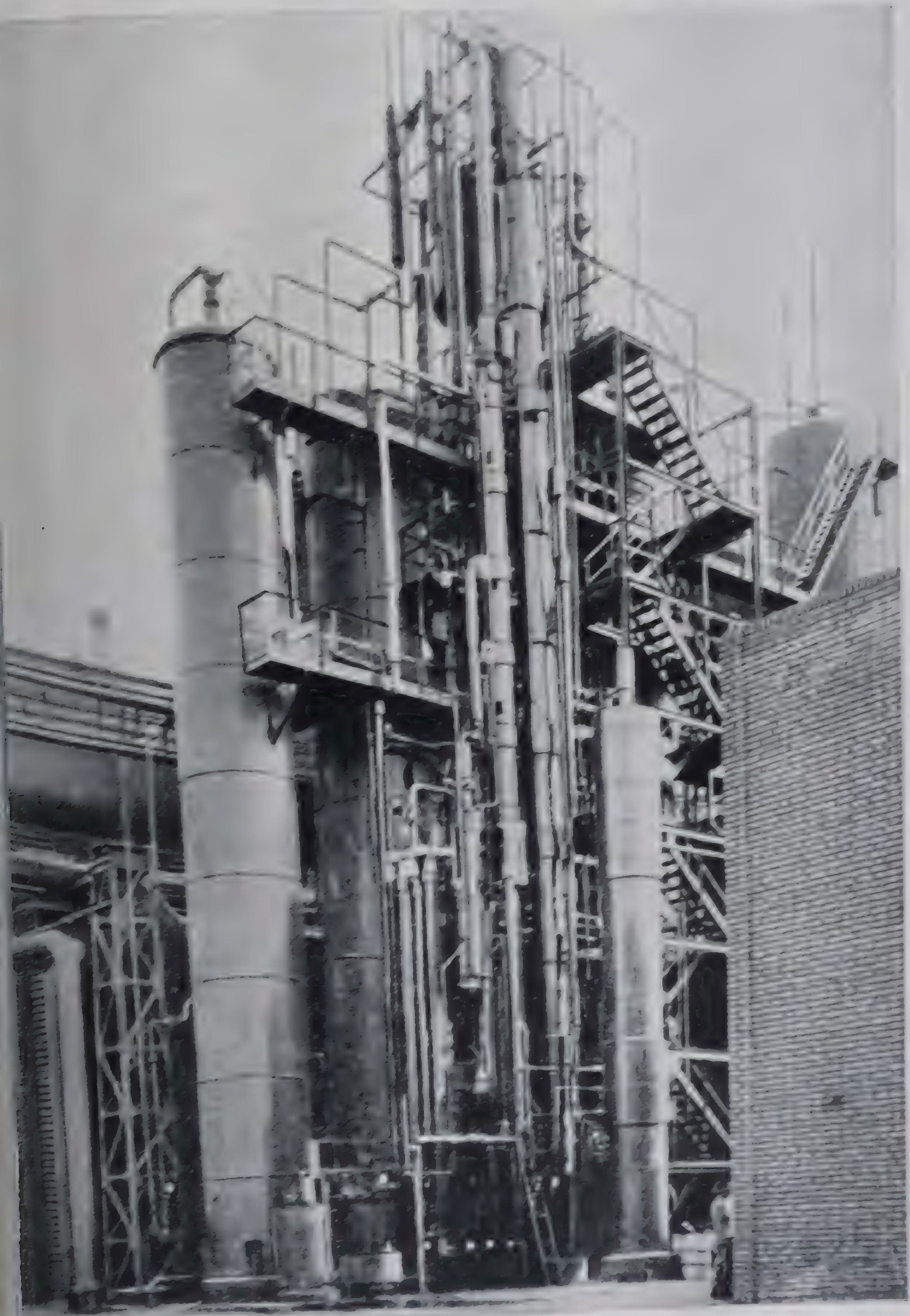


FIG. 11—ANOTHER VIEW OF THE PILOT PLANT FOR DEPHENOLIZATION OF LIQUORS

The ammoniacal liquor from the reserve tank (1) filtered through quartz, flows at a temperature of 70°C. into the upper section of the extractor (2). Simultaneously, the solvent after passing through a preheater (4) enters this vessel near the bottom counter-current to the liquor, thereby, the solvent takes up the phenol dissolved in the liquor. The water from the extractor (2) flows into the separator in which the rest of the solvent is separated, and then it leaves the plant. The phenol-enriched solvent is freed from its water content in vessel (5). Further, the solvent passes through the intermediate vessel (6) and heat-exchanger (7) into the dehydration column (8) where, with the help of an inert gas (nitrogen, air), it is freed from its small contaminated water. The solvent freed from water, runs through the intermediate tank (9) into the rectification column (10) kept under reduced pressure, at the top of which raw phenolic compounds are recovered. The solvent, containing phenol flows from the base of the column (10) into the intermediate tank (11), and from there is conducted into the stripping column (12), which likewise is kept under reduced pressure. The top product of the stripping column is mixed in the intermediate vessel (9) with the enriched dewatered solvent, and then flows back into the rectification column (10).

The dephenolized solvent runs from the base of the column (12) into the tank (13) and then over a heat-exchanger (7) and cooler (14) into a separator (15), from the base of which tar components can be taken out.

The solvent from the separator (15) flows via the tank (3) into the extractor (2) and thus returns to the process.

The first dephenolization plant for ammoniacal liquors with a capacity of 450 cu.m. water per hour and working on this principle, has been recently constructed in the Ruhr area.

For the economic recovery of highly pure phenolic compounds, the phenols obtained from waste liquor are mixed with the tar oils containing phenol and, they are treated together in a tar oil dephenolization plant, whereby, as stated earlier, phenolic compounds with a purity of 99·8 per cent can be obtained.

Figs. 5, 6, 7, 8 and 9 show different views of the Pilot Plant for the dephenolization of tar and Figs. 10 and 11 show the Pilot Plant for the dephenolization of liquor.

GENERAL DISCUSSION

Dr M. G. Krishna: I wish to make some general comments on the papers presented from our laboratory on the processing of l. t. tar. The economics of l. t. c. industry is largely dependent on the utilization of the main byproduct, the l. t. tar. Our approach to the problem can be classified under two types; the short-term and the long-term methods of utilization.

No commercial scale l. t. c. plants are at present in operation in India. It is, however, expected that several such plants will be established in the near future. Our laboratory therefore considered it necessary as a short-term measure, to prepare the ground by evolving processes for the preparation of readily marketable products from l. t. tar. Products similar to these from high temperature tar which are now in market should be prepared from l. t. tar and their marketability studied so that the l. t. c. industry will not have to face the initial troubles of survival.

For this purpose, mostly conventional processes have been used for the preparation of road tar and of wood preservative creosote and disinfectants. The road tar produced from l. t. tar at the Regional Research Laboratory has been tested by Central Road Research Institute, Delhi. The Indian specifications for timber creosote are based on h. t. tar. In the United Kingdom and New Zealand specifications have been modified to include products from l. t. tar also. The sample prepared by this Laboratory has been tested by Forest Research Institute and according to a recent paper [*J. sci. industr. Res.*, **20D** (1961), 273] this material has been found to be quite satisfactory. It is hoped that in due course the specifications will be suitably modified. Considerable work on the colour removal problem for disinfectant preparation has been done at the Coalite Works in the United Kingdom. We have also been able to produce a creosote giving white emulsions. Other important problems concerning treatment of l. t. tar are the extraction of tar acids and conversion of tar oils to liquid fuels by hydrogenation. It is necessary that these materials should be produced as soon as the l. t. c. industry is started, so that the industry does not face the problem of disposal of tar.

Under the long-term programme, other aspects such as production of electrode binder, cracking, solvent extraction, etc. should be considered. One interesting point worth considering is to combine l. t. c. with production of h. t. tar. The tar vapours from l. t. c. plants can be further cracked to yield a product corresponding to h. t. tar. Work on secondary thermal treatment of l. t. c. gases is being carried out in other countries. These aspects require consideration with a view to improve the economics of l. t. c. industry.

Dr H. S. Rao: In the proposed utilization of tar, there appears to be a gap with regard to neutral oil. A detailed examination of neutral oil from l. t. tar was done at C. F. R. I., and about 100 compounds were detected and a few have been estimated. From these studies, three broad patterns of utilization of neutral oil arise. Neutral oil contains some of the α- and β-substituted naphthalene hydrocarbons and these on oxidation yield phthalic acid. Therefore, when a particular cut of neutral oil is oxidized, phthalic acid can be obtained. Secondly, it may be possible to use a portion of the neutral oil as wash oil for benzole recovery. Thirdly, blending of the neutral oil with inferior grade kerosene and diesel oil can also be tried.

Dr M. G. Krishna: I wish to comment on this last point of Dr H. S. Rao on the utilization of neutral oil. Kerosene as it is marketed consists of paraffinic, naphthenic, olefinic and aromatic hydrocarbons. Neutral oil also contains these hydrocarbons. The R. R. L. evolved a method to make illuminating fuel from the neutral oil by solvent extraction and a patent on this method has been applied for.

Shri M. C. Bakshi: The Bengal Chemical & Pharmaceutical Works Ltd, are also employing a method for the disposal of the tar similar to that described in one of the papers, i.e. distillation and preparation of road tar. After recovering the tar acids, neutral oil is used for fuel purposes. The tar fraction giving red colour is mixed with heavy oil and used as wood preservative. The pitch is blended with higher boiling tar oils from coke ovens and not with low temperature tar as mentioned by Shri Bagchee. Tars or pitch from h. t. c. and l. t. c. even though having the same utlimate analysis, may differ in molecular weight. When applied on the road, there is the possibility of polymerization and breakage. This should be kept in mind while preparing road tar from l. t. tar.

In my opinion there is no competition between h. t. and l. t. tars, since they have independent market. It is, however, necessary to evolve new lines for utilization of l. t. tar so that the economics of l. t. c. may be improved.

Dr M. Vahrman: I should like to make a few general comments on the processing and utilization of l. t. tar and its products.

L. t. c. has been undertaken hitherto (and the same applies to the projects contemplated), for the production of a solid product or char, the markets for which are known in advance with some degree of exactitude. Low temperature tar, on the other hand, has to make its way in a field which has been dominated by the high temperature product, and, increasingly, by petroleum. The economics of its utilization are not known so exactly, especially as the chemical scene is a rapidly changing one.

It is evident that a great deal more needs to be known about the inter-related subjects of its composition, and its rational treatment and utilization. L. t. tar may be a chemist's dream in its richness and variety of components, but it is often the commercial man's nightmare. At present, it seems that the full utilization of the tar is bound to lag behind that of the solid product in any new venture. This is why those responsible for a utilization programme must plan on its being made up of different stages, not necessarily representing an exact chronological sequence, but overlapping with one another in various ways.

First, there is the preparation and utilization of bulk products—the tar itself as simple blends, creosote, pitch, crude tar acid fractions—with little processing, and that by conventional means. This stage, mainly involving a consideration of existing markets or finding substitutes for or improvements of existing products may be a great help in starting up a commercial l.t. tar programme, satisfying immediate commercial exigencies, and providing a breathing space for further work to be done.

Second, there is the further refining of fractions to obtain narrower cuts or crude or pure chemicals (for example, the refining of phenols and the preparation of marketable derivatives from them).

Third, there is the processing of l.t. tar and its derivatives by means appropriate to its peculiar composition (e.g. by solvent extraction, in addition to distillation) with the simultaneous development of new markets for the products. It is here that it may begin to come on to the scene much more as a material in its own right, and when the patient chemist's dream may be realized. It is probably unnecessary for me to stress that all this requires further research and an extension of utilization work to comprehend the finding of appropriate *new* uses for specific l.t. products.

Dr R. Vaidyeswaran: I am interested to know more about the suggestion of Dr H. S. Rao regarding the blending of neutral oil with kerosene and diesel oil particularly with regard to the proportion and type of neutral oil ? In my opinion neutral oil as such may not be suitable for blending. It has to be hydrofined or subjected to similar treatment. In the Coalite works, till recently, the neutral oil after acid treatment was being mixed with diesel oil; treatment with hydrogen is now thought of.

Dr H. S. Rao: The blending of neutral oil with diesel oil suggested by me is only an idea. As to which fraction should be used and in what proportion, depends on the integrated programme of utilization of neutral oil and also which cut of neutral oil is to be used for phthalic acid manufacture.

Dr M. G. Krishna: Direct burning of tar has been suggested as an immediate solution to the problem of its disposal. In India an important steel company is burning all the high temperature tar it produces. It is a matter which depends on the general industrial development of the country and how one views the problem of byproduct disposal.

Dr S. K. Sircar: I feel that while one has to consider the suggestions for long term utilization, the immediate solution may be to remove the tar acids and use the neutral oil instead of the high temperature tar, as fuel oil, since the h.t. tar industry is well developed, and the outlet for similar products from l.t. tar is not well established.

SECTION FOUR

Survey, Economics and Statistics of L.T.C. Products

Electricity—A Byproduct of Low Temperature Carbonization of Coal

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The Indian energy economy will be substantially based on coal even by 2000 A.D. With increasing cost of mining coal, the cost of electrical energy will also increase. In order to generate electricity from coal at competitive prices, the only alternative appears to be to carbonize non-caking coal at low temperatures, recover and process the liquid and gaseous byproducts and use the pulverized char as fuel. Thus electricity will be one of the byproducts of low temperature carbonization of coal.

Electricity is the most versatile form of energy and can be easily transmitted over long distances. The kinetic energy of water through the pen stock pipes, the chemical energy stored in coal and petroleum, nuclear energy and solar and geothermal energy can be converted into electrical energy. The per capita consumption of electrical energy is an important index of the industrial activity and material prosperity of a nation.

ENERGY DEMANDS

The estimates of National Council of Applied Economic Research for the installed capacities of thermal, hydro, petroleum and nuclear power stations during 1960-75 are given in Table 1.

The estimated gross consumption of energy from different sources for 1960-75 is given in Table 2.

It is obvious, therefore, that even towards the end of this century 55-60 per cent of India's energy demands would be met from coal.

TABLE 1—ESTIMATED INSTALLED CAPACITIES OF POWER STATIONS

(million kw)

Year	Thermal	Hydro	Petroleum	Nuclear	Total
1960	3·72	2·92	0·30	—	6·94
1965	6·40	5·60	0·50	0·25	12·75
1970	10·46	10·00	0·78	0·82	22·06
1975	16·48	16·76	1·26	1·92	36·42

TABLE 2—ESTIMATED GROSS ENERGY CONSUMPTION

(%)

Year	Coal	Hydro	Petroleum	Nuclear
1960	76·5	10·6	12·9	—
1965	74·5	11·9	13·0	0·6
1970	72·5	12·6	13·2	1·7
1975	71·2	12·6	13·9	2·3

TABLE 3—YEARLY VARIATION OF PRICE OF COAL PER TON

Year	Rs per ton
1955	15·96
1956	17·62
1957	19·87
1958	21·87
1959	21·94
1960	22·81
1961	22·87

PRICE OF COAL

The fuel used for power generation would be the noncoking coal and carbonized lignite residues, as coking coals would be reserved exclusively for the expanding steel industry. It has been estimated that by the end of this century the demand for steel in our country would be about 110 million tons per year equivalent to a per capita consumption of 130 kg. which is the current figure for Japan and Italy. The quantity of coking coal required would also be about 110 million tons per annum.

The cost of mining coal is steadily going up as shown in Table 3.

The present cost of generation of electricity with coal at Rs 22/ton is 3·0-3·5 nP per unit from medium capacity power stations. For small generating stations, remote from coalfields, the cost of generation is as high as 10-13 nP per unit. It is now becoming a practice to set up big thermal generating stations of about 300-500 Mw at the pit heads. This would considerably relieve the strain on the railways in the movement of large quantities of coal. It is far easier to transport electricity from pit head to large industrial areas than to transport coal.

LOW TEMPERATURE CARBONIZATION

Coal will continue to be the chief industrial fuel for generating electricity till the end of this century. As the cost of mining coal is likely to increase, the only possible way of generating electricity from it at a price competitive with hydro power would be to use a byproduct fuel from coal The two known methods at present of getting byproducts from coal are the high and low temperature carbonization of coal. High temperature carbonization is used for making metallurgical coke from good coking coals or blends of coking and feebly coking coals. L.t.c. yields semicoke, tar, tar acids and a rich gas. The semicoke contains about 10 per cent volatiles and after pulverizing would be a good fuel for steam raising in power stations.

Coal tar is another important byproduct from l.t.c. The whole of the tar can be hydrogenated under medium pressures to produce Diesel fuel. It has been estimated that India would be short of Diesel fuel by 1·63 million tons per annum during the Third Five Year Plan period; part of this deficit could be met by hydrogenation of tar from l.t.c. plants.

The gas contains a high percentage of unsaturated hydrocarbons which could be converted into ethylene and propylene for the manufacture of high polymers. The gas could also be reformed with steam to produce hydrogen for ammonia synthesis or can be cracked to produce carbon black. The exact utilization of the gas would largely depend upon the trends of the petro-chemical industry in the country.

SEMICOKE AS AN INDUSTRIAL FUEL

The capital cost of a plant of a carbonizing capacity of 2000 tons of coal per day is about Rs 30 million. The expenses and returns for a plant of this capacity are indicated in Table 4.

If the middle oil can be hydrogenated, and the phenolic constituents be further processed and refined the returns on these items would be much more.

The semicoke weighing 1330 tons would therefore cost Rs 17,000 (64,000-47,000). Out of the 1330 tons, if 130 tons are sold as domestic fuel at Rs 40/ton, the cost of 1200 tons of semicoke to be used as an

TABLE 4—EXPENSES AND RETURNS OF L.T.C. PLANT
(Coal capacity: 2000 tons/day)

	Rs
DAILY EXPENSES OF THE L.T.C. PLANT	
Cost of 2000 tons of coal at pit head at Rs 22/ton	44,000
Operation charges (taken at 20% of the capital investment)	20,000
Total daily expenses	64,000
DAILY RETURNS	
Sale of 4000 gal. of light oil at Re 1/ gal.	4,000
Sale of 36,000 gal. of middle oil at Re 0·75/ gal.	27,000
Sale of 40,000 lb. of phenolic constituents at Re 0·40/ lb.	16,000
Total daily sales	47,000

industrial fuel for generating electricity would cost Rs 11,800 or Rs 10/ton. On a conservative estimate of 2 lb. of coal per KWH (the average for a big modern power station is 1·25 lb./per KWH), 1200 tons of coal per day would generate 50 MW. The cost of fuel per KWH would work out to 0·9 nP. The depreciation on plant and machinery and the working expenses will work out to 0·6 nP per unit, so that the net cost of generation would be 1·5 nP per unit. This rate is quite competitive with that of hydro-energy.

The location of power stations in the country may be planned as follows: Regions which have good water resources like Kerala and Mysore should have a network of hydro stations; regions where coal is available like Madhya Pradesh, Bihar and Andhra, should have big thermal stations at pit heads; and regions remote from both these natural resources should have nuclear power stations. Planning on these lines would generate cheap power, cut down power costs in industrial production, and help the growth of electro-chemical and electro-metallurgical industries.

SECOND LOOK

There has been a lot of shyness and resistance on the part of the government and private industry in setting up big l.t.c. units, for the economics of the industry was one sided, based entirely on the utilization of semi-coke for domestic purposes. With the demand for cheap power from the rapidly growing industries in the country, the serious shortage of diesel fuel in the coming plan periods, and the growth of the chemical industry that is envisaged in the near future, the l.t.c. industry assumes a multi-purpose dimension and the economics of the industry is brighter than before. The planners should, therefore, have a second look at it and give an impetus to an industry, the economics of which has long been doubted.

Pattern of Domestic Fuel Consumption in South India

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Neyveli Lignite Corporation

Neyveli

The problem of domestic fuel requirements of South India, the influence of low temperature carbonization, gas and byproducts as replacement of present day fuels and its impact upon the food production and industrialization of this region is discussed.

The standard of living of the people, the degree of industrialization and per capita income of a nation are directly related to the per capita consumption of energy. India with its per capita consumption of all forms of energy of about 0·5 tons of coal equivalent ranks amongst the most underdeveloped countries of the world. Typical data on per capita consumption of energy and annual income are given in Table 1.

The pattern of energy production and consumption in India is rather primitive and even this low figure of about 0·5 ton per head per year is derived mostly from wood fuel and farm wastes.

India, with a population of 80 per cent farmers and 41 per cent of land under cultivation, as compared to the world average of 10 per cent, produces less foodstuffs than most of the countries of the world, and has to depend upon imported food grains. The increasing population poses a large number of problems with regard to food and fuel supply. There is an imbalance between the rate of population increase and food production.

The problem requires that all the energy resources of India should be conserved and utilized in the most efficient manner. The present average figure of efficiency of fuel consumption in India is barely 6 per cent. The present consumption of energy is less than 100 therms per head per annum, equivalent to 200 million tons of coal for the entire country. The requirements of the domestic sector alone are about 100 million tons. Out of this 100 million tons of coal equivalent that goes into the hearth, barely 2-3 million tons are met by coal. The contribution of kerosene and

TABLE 1—PER CAPITA ENERGY CONSUMPTION AND ANNUAL INCOME

COUNTRY	PER CAPITA CONSUMPTION (coal equivalent) Tons	ANNUAL INCOME Rs
U.S.A.	10	11,000
Canada	7	6,600
United Kingdom	6	5,400
Belgium	4	3,700
Netherlands	2·5	2,500
Japan	1·0	1,100
India	0·4	300

electricity is of the same order. The balance is met by wood, dung, charcoal and farm waste. It is essential from the point of view of soil conservation, flood control and food production that a switch over be made from secondary fuels to fossil fuels.

In the absence of large reserves of fossil fuels and the transport bottlenecks, the problem acquires greater significance in South India. The population of South India, comprising the four States of Madras, Andhra, Kerala and Mysore, is about 110 million. The energy requirements at a bare minimum of 80 therms per head works out to 40 million tons of coal equivalent per annum. Electric power, hydro and thermal, contribute to about 4-5 million tons of coal equivalent and petroleum products another 3-4 million tons of coal equivalent. Assuming the energy content of cowdung of a normal cow as 16 million B.t.u. per annum and that 40 per cent of the total quantity of cowdung is used as fuel, the annual consumption of cowdung approximates to 180 million tons of green (36 million tons dry) or approximately 20 million tons of coal equivalent. The railways consume nearly 4-5 million tons of coal. The balance of about 8 million tons is met by wood, charcoal and farm waste. This corresponds to about 20 million tons of wood. Assuming a yield of 2000 tons of wood per acre, it involves a deforestation of about 10,000 acres per annum. Wood is felled to meet not only the domestic requirements, but for industrial use as well. Till recently, wood charcoal was used for reducing iron ores in Bhadravati Steel Works. Fertilizers and Chemicals (Travancore) Ltd, alone consume nearly 350 tons of wood per day. The per capita consumption of wood as domestic fuel and for industrial purposes is in the proportion of 1:1 in India as against 1:5 in United States and 1:3 in Germany. It is, therefore, necessary to reduce the use of wood and farm waste for fuel.

An adequate supply of domestic fuels is, therefore, a prerequisite if agricultural development through afforestation, use of fertilizers, organic manure and modern techniques of cultivation are to be made possible.

Railways at present use high grade coal. The efficiency of steam traction is hardly 4-5 per cent as compared to 18-20 per cent for diesel traction. This puts a great strain on the limited and fast depleting reserves of good quality coal. Also, coal has to be transported from a distance of over thousand miles engaging a lot of rolling stock, thus straining further the already overcrowded transport system. Recently, a committee of the Railway Board recommended that 50 per cent of the track be electrified and 30 per cent dieselized, keeping for steam traction only about 20 per cent.

The cost of electrification of tracks is rather heavy and necessitates large quantities of cheap surplus power. The hydro-resources of Madras State have been harnessed practically to the maximum and the State has to depend upon power from outside. The frequent power cuts, power shortage and high cost of electrification will hardly justify electric traction except in very special cases.

The only alternative is diesel traction for which at present we have to depend upon imported petroleum products which will adversely affect the balance of payment position.

Production of low temperature (l.t.) coke will on the one hand replace charcoal and kerosene oil consumption in the urban areas and on the other will yield tar from which diesel and other fuel oils can be produced. On carbonization a ton of coal yields diesel oil equivalent to a ton of coal in use besides yielding large quantities of various grades of phenols which can serve as the basic raw material for starting a chain of chemical industries. At present there is little production of phenols in the country and we have to depend upon imported materials. India imported about 1,000 tons of phenols in 1959 and this demand is likely to increase four-fold by the end of the Third Five Year Plan.

Fig. 1 shows the two proposed zones in South India where low temperature carbonization (l.t.c.) plants can be located. A modest beginning in this regard has already been made at Neyveli.

Recent experiments at the National Metallurgical Laboratory, Jamshedpur, on the use of l.t. coke from Singareni coal reveal that the coke is economically suitable for smelting and reduction of rich iron ores. Results of preliminary experiments on the use of lignite char for the reduction of iron ore are encouraging and it is proposed to send 2,000 tons of lignite in October this year to East Germany and Norway for conducting large scale tests.

All the industrially advanced countries use gas for their industrial and domestic requirements. It is worth considering to connect the overcrowded large cities with a population of over 0·5-1·0 million with a gas grid by transmission of gas from plants situated in the coal bearing areas. This would not only prevent wasteful transport of solid fuels by rail but will also yield tar which can be processed to yield diesel oil, etc. thus supplementing the liquid fuels from l.t.c. of coal. Stringent health

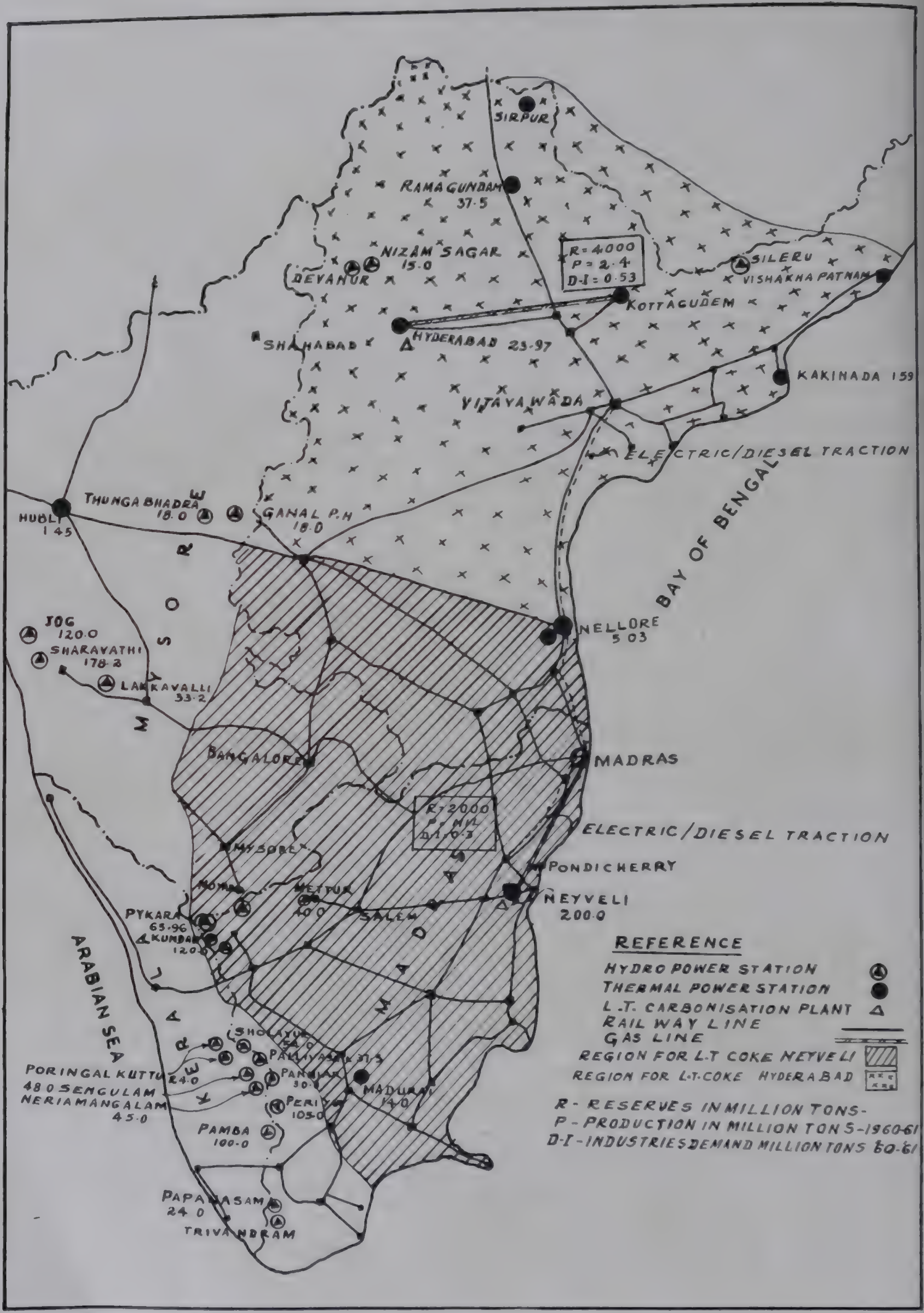
SIRPUR
RAMAGUNDAM
37·5
NIZAM SAGAR
15·0
DEVANUR
R = 4000
P = 2·4
D·I = 0·53
SILERU
VISHAKHA PATNAM
KOTTAGUDEM
SHAHABAD
HYDERABAD 23·97
KAKINADA 159
VIJAYAWADA
ELECTRIC/DIESEL TRACTION
BAY OF BENGAL
HUBLI
1·45
THUNGA BHADRA
18·0
GANAL P.H
18·0
MYSORE
JOG
120·0
SHARAVATHI
178·2
LAKKAVALLI
33·2
NELLORE
5·03
BANGALORE
MADRAS
R = 2000
P = Nil
D.I = 0·3
ELECTRIC/DIESEL TRACTION
MYSORE
PONDICHERRY
NEYVELI
200·0
METTUR
40·0
SALEM
MADRAS
PYKARA
63·96
KUNDAH
120·0
ARABIAN SEA
KERALA
SHOLAYUR
54·0
PALLIVASAL 37·3
PORINGAL KUTTU 24·0
48·0 SENGULAM
NERIAMANGALAM
45·0
PANNIAR
30·0
PERIYAR
105·0
MADURAI
14·0
PAMBA
100·0
PAPANASAM
24·0
TRIVANDRAM
REFERENCE
HYDRO POWER STATION
THERMAL POWER STATION
L.T. CARBONISATION PLANT
RAIL WAY LINE
GAS LINE
REGION FOR L.T COKE NEYVELI
REGION FOR L.T.COKE HYDERABAD
R - RESERVES IN MILLION TONS -
P - PRODUCTION IN MILLION TONS - 1960-61
D-I - INDUSTRIES DEMAND MILLION TONS 60-61

FIG. 1—MAP OF SOUTH INDIA

laws, high efficiency and premium for the fuel will go a long way to meet the cost of laying pipe lines. A modest beginning can be made by locating the plants at Singareni and Neyveli. The Neyveli grid can serve Pondicherry and Madras, while either a gas line from Singareni or a total gasification plant in Hyderabad city will meet the demand of Hyderabad. The two fuels, l.t. coke and gas are in reality, complementary.

ECONOMICS

In addition to the above mentioned factors, a survey of the price index of various fuels in Madras State indicates that gas and l.t. char can easily meet the competition from other fuels. The price of wood and charcoal, the most common fuels in use in urban areas, is steadily rising, as shown in Fig. 2.

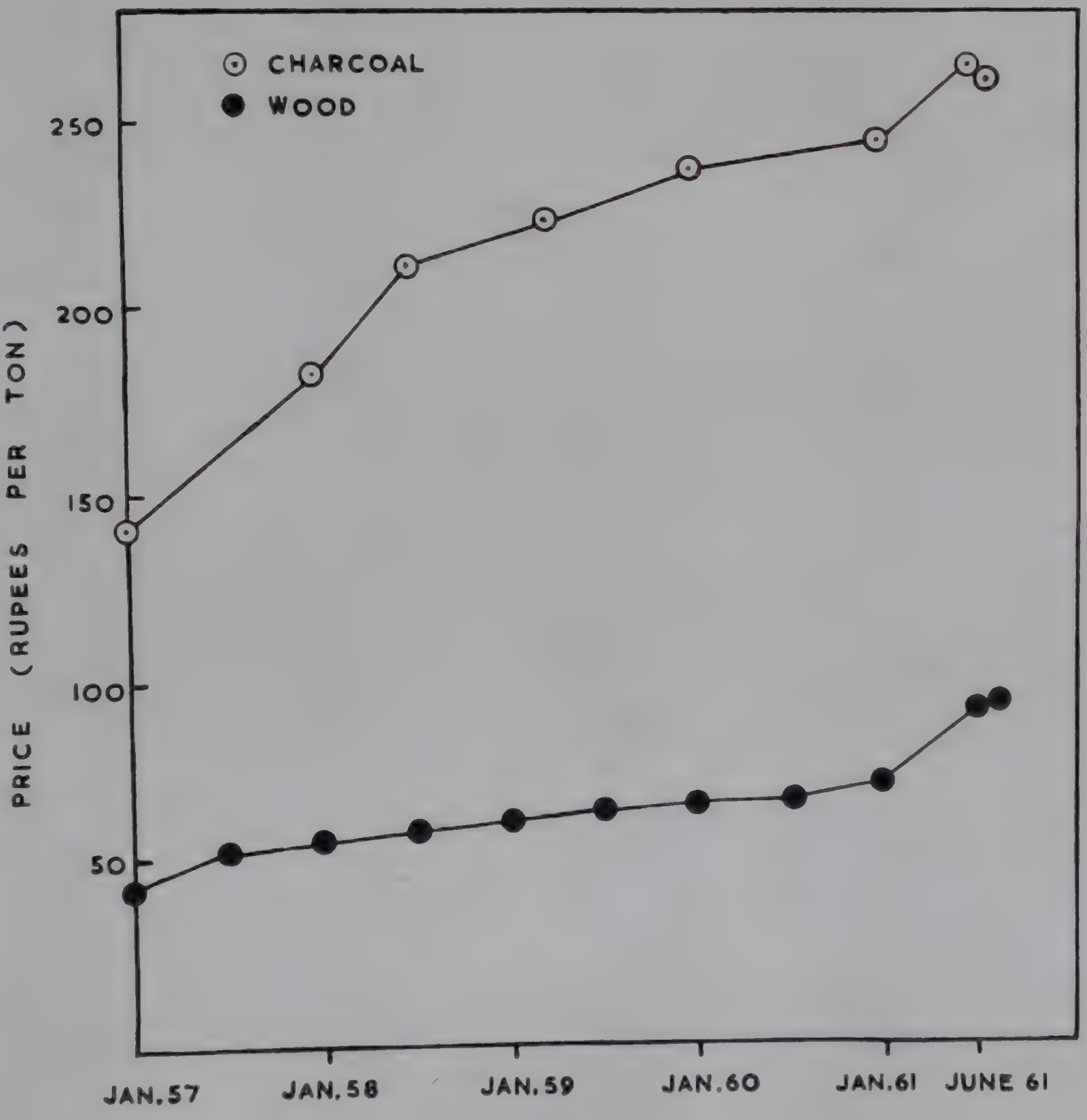

Fig. 2—Price of domestic fuels

TABLE 2—EFFECTIVE PRICES OF DOMESTIC FUELS*

FUEL	CALORIFIC VALUE kcal./kg.	EFFICIENCY %	MARKET PRICE PER TON Rs	EFFECTIVE PRICE nP/1000 cal.
Charcoal	7,100	28	252·60	12·70
Wood (dry)	4,708	17	91·00	11·36
Cowdung	2,127	11	66·00	27·78
Kerosene	10,780	48	0·34/litre	8·07
Electricity	..	76	0·15/KWH	22·90
Gas	4,200	60	159/1000 Nm³	6·30
Lignite char	6,900	35	i) 150·00/ton ii) 200·00/ton	6·21 8·28
Soft coke	6,300	32	60·20/ton	2·98

*Price Index, Madras, July 1961.

Several investigations have been conducted in the laboratory at Neyveli on the use of the lignite char as a domestic fuel. These investigations have shown that lignite char is in every way a superior fuel to charcoal. The fuel is smokeless, odourless and can ignite quite easily. It was also found that there was an economy of 25 per cent by weight if char is used as domestic fuel. Results of these tests have already been published elsewhere . Various fuels were used in domestic ovens and efficiency calculated. The effective prices of various fuels (Table 2) show that gas and lignite char despite their high market price are the cheapest fuels after soft coke. Soft coke has to be transported all the way from coalfields and the supplies are intermittent and limited. At present, there are practically no consumers of this fuel in the domestic sector.

ACKNOWLEDGEMENT

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Low Temperature Carbonization Potentialities in Madhya Pradesh

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Use of cowdung, a valuable organic manure, as a domestic fuel and use of charcoal have led to the impoverishment of soil fertility in India. The remedy is to find a suitable substitute fuel. Semicoke by low temperature carbonization is the only answer. Of the many important processes such as, the Krupp-Lurgi, the Disco, the Hayes and the 'Lurgi Spuelgas', the 'Lurgi Spuelgas' process is recommended being the cheapest and easy of operation. Madhya Pradesh has enormous reserves of noncoking coal suitable for low temperature carbonization. From the point of availability of raw materials, thermal power and a nearby ready market, locating the l.t.c. plants at Pathakhera, Amlai and Singrauli is recommended. The cost of production of semicoke is estimated at Rs 41 per ton.

It has been estimated that India consumes 80 million tons of cowdung per year as domestic fuel. Cowdung is an eminently suitable organic manure, the right place for which is the impoverished agricultural fields needing more manure. The return of this manure to the soil can be ensured only by finding an easily available substitute fuel. Low temperature carbonization (l.t.c.) of coal appears to be the only way to meet this desideratum, even if it has to be subsidized in the beginning, before the technique of economically processing of the resultant tar is successfully mastered and the plant and equipment for the purpose indigenously manufactured. Another insidious process leading to the impoverization of the land is the production of charcoal. The indiscriminate destruction of forests, both in the watershed areas and elsewhere for the production of charcoal has resulted in the denudation of the fertile top soil and in devastating floods which later aggravate soil erosion. The extent can be gauged for example from the fact that at present in Madhya Pradesh more than one train-load of charcoal is being despatched from the Betul-Ghoradongri-Bhopal area to destinations around Delhi and Bombay. One ton of charcoal requires about 5 tons of forest growth covering 0·0025 acres of forest land. Here also the remedy is a cheap easily available fuel produced by l.t.c. of our abundant non-caking coals of different grades.

As a domestic fuel charcoal is preferred because of its high reactivity, smoke-free burning and higher calorific value (about 15 per cent higher than industrial coke resulting from its low ash content). The low ash content is, however, not always a scoring point for domestic fuel as a certain amount of ash is of use to maintain the glow of fire and in slowing down the rate of combustion by throttling the access of air after the initial heating is over.

Carbonization processes which are carried out at temperatures between 450 and 700°C. are classed as l.t.c. processes. The principal products are a semicoke or char, equivalent to about 70-80 per cent of the coal and 15 to 30 gal. of tar per ton of coal. In addition, several thousand cubic feet of gas and 2·5 to 3 gal. of light oil are usually produced per ton of coal carbonized.

L.t.c. is practised with the primary object of producing a semicoke which is suitable for domestic or boiler use or for replacement of low-volatile coal in blends with high volatile coal used in high temperature (h.t.) carbonization.

L.t.c. also represents the first step in the complete gasification of coal. The second step is gasification of the l.t. coke in a producer or water gas plant. The water gas is suitable for the synthesis of oils by the Fischer-Tropsch process. During the Second World War, Germany manufactured a large proportion of her fuel and lubricating oil requirements from l.t. tar and from water gas made from coke. In India, during the Second World War gas producers were installed in automobiles and trucks which were based on charcoals but could have been replaced by semicoke.

The l.t.c. process possesses two advantages over the h.t. carbonization, viz. (1) reduction in the capital cost due to substitution by steel for refractory brick work in the retort walls, and (2) reduction in the operating cost because less heat is required to raise coal to the lower carbonizing temperature.

L.t.c. of coal is done by various processes important amongst which are the Krupp-Lurgi, the Disco, the Hayes, and 'Lurgi Spuelgas' processes, as described by Parry[9].

L.t.c. can be carried out either by external heating of the retort containing fine coal at rest or in motion; or by internally heated vertical retorts. In the 'Krupp-Lurgi' retorts the fine coal is at rest and heat penetrates from the walls to the centre of the charge and the product is discharged as a lump coke.

In the Disco process fine coal is introduced into one end of a revolving retort and heated by contact with its heated surface. Although the char or coke from this process has special form, value and reactivity, it is too costly for boiler plant fuel because of the high investment cost.

In the Hayes process the externally heated retort is rotated slowly in one direction and the fine coal is propelled through it by screws which rotate forward and backward to move the coal at the desired rate. The char produced is manufactured into briquettes for domestic fuel.

In the well-known 'Lurgi-Spuelgas' system of carbonization, a combustible mixture of fuel gas and air is burnt in a burner near the base of the column and the hot products of combustion rise upward through the descending material heating it to carbonizing temperature. The carbonized material is cooled by counter-current circulation of gas below the burner. The coal distils as it is heated to the range of 400 to 482°C. and the vapours move upward through the charge as a mist. These retorts operate with relatively low off-take temperature of out-going gas because of the persistence of the tar mist. The thermal efficiency is relatively high and minimum equipment for condensing the vapour after leaving the retort is required.

Such retorts operate best on closely sized materials which encourage even distribution of the heating gases. They cannot operate on coking coals. This process appears to be most suitable for the production of domestic fuel in India and the plant has few moving parts and its operation is easy.

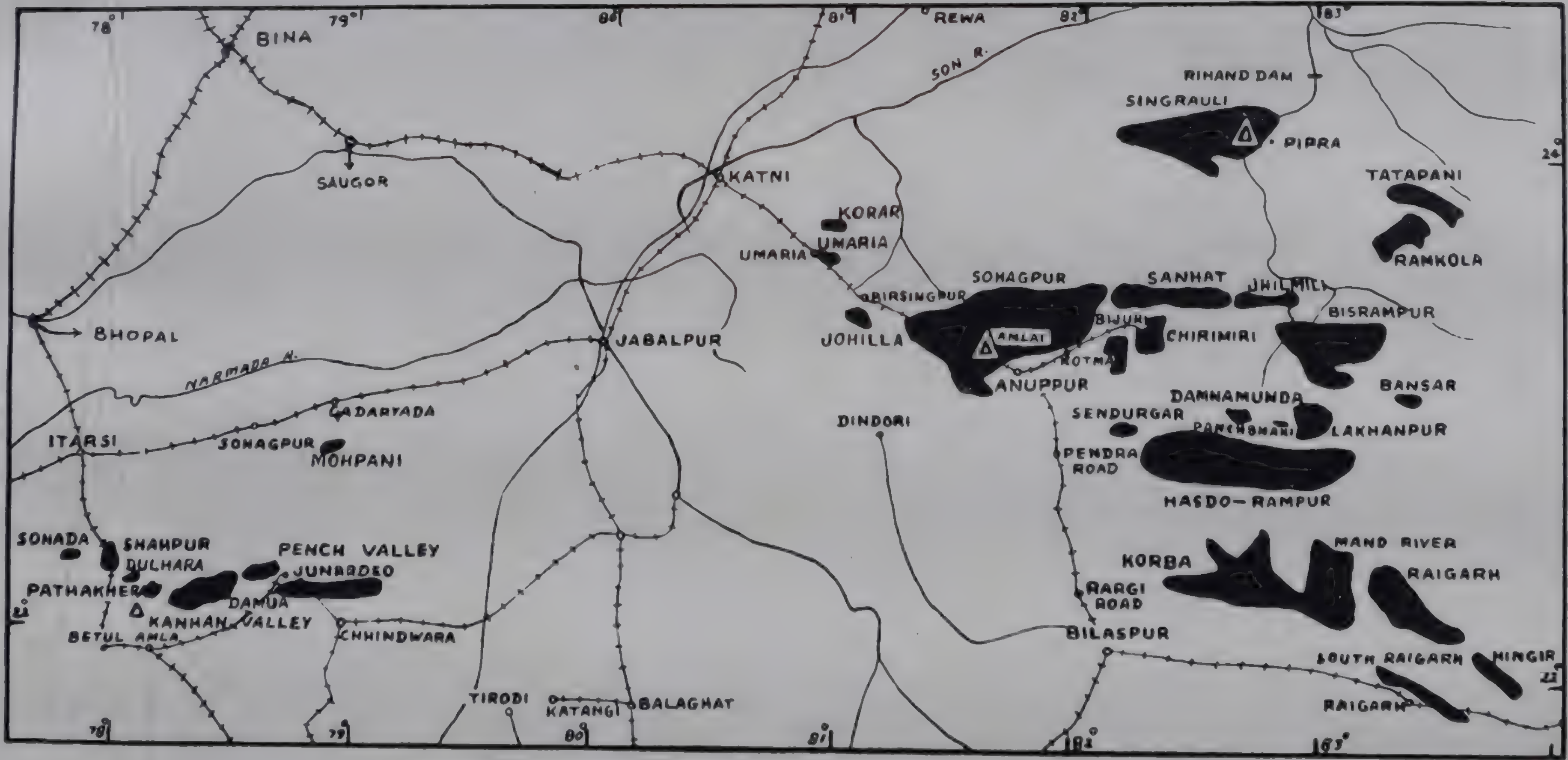
Madhya Pradesh is endowed with vast reserves of noncoking coal eminently suitable for l.t.c. Most of the coal found in the various coalfields of Madhya Pradesh (Fig. 1) falls within the type desired for l.t.c. Names of the important coalfields of Madhya Pradesh are given in Table 1, along with their reserves and analysis[4,6].

The following are the important considerations when proposing a site for the plant.

1. Adequate quantity of coal of suitable quality should be available near site
2. Proximity to a thermal power station
3. Nearness to a large market.

Quality of the Coal. The coal should preferably be non-caking and not have a high ash content as after carbonization the ash content in the coke rises and results in unnecessary railway freight on inert material and difficulties in the disposal of the cinder.

Size of the Coal. As sized coal namely 2-6 in. is to be used an outlet must be found for the slacks. Generally 20 per cent of the run of mine is slack. Further if any transportation of the sized coal is involved the slack formed during transportation will be of the order of 10 per cent. Where the carbonization plant is located near a thermal power station the sizing can be done at the plant and the slacks delivered to the power station. The power requirements of the l.t.c. plant can be met from the power station thus avoiding the capital outlay on an independent power plant.


78°
79°
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24°
21°
BINA
REWA
SON R.
RIHAND DAM
SINGRAULI
PIPRA
TATAPANI
RAMKOLA
SAUGOR
KATNI
KORAR
UMARIA
UMARIA
BIRSINGPUR
SOHAGPUR
SANHAT
JHILMILI
BISRAMPUR
BHOPAL
JABALPUR
JOHILLA
AMLAI
BIJURI
CHIRIMIRI
KOTMA
ANUPPUR
BANSAR
NARMADA R.
GADARWADA
DAMNAMUNDA
SENDURGAR
PANCHBHAINI
LAKHANPUR
DINDORI
ITARSI
SOHAGPUR
MOHPANI
PENDRA ROAD
HASDO—RAMPUR
SONADA
SHAHPUR
PENCH VALLEY
DULHARA
JUNARDEO
MAND RIVER
KORBA
RAIGARH
PATHAKHERA
DAMUA
KANHAN VALLEY
KARGI ROAD
BETUL AMLA
CHHINDWARA
BILASPUR
SOUTH RAIGARH
HINGIR
TIRODI
KATANGI
BALAGHAT
RAIGARH

FIG. 1—COAL FIELDS OF MADHYA PRADESH SHOWING PROPOSED SITES FOR LOW TEMPERATURE CARBONIZATION PLANTS

TABLE 1—SOURCES, RESERVES AND ANALYSIS OF COALS FROM MADHYA PRADESH

(based on data available from G.S.I. and F.R.I.)

NAME OF COALFIELD	RESERVES (million tons)	PROXIMATE ANALYSIS (% air-dried basis)			
		Moisture	Ash	V.M.	F.C.
Pench Valley	114 (I.C.C. 1946)	4-10	15-20	28-34	44-56
Kanhan Valley	66 (semicoking only) (G.S.I. 1950)	2-5	15-19	28-33	41-51
Tawa Valley Pathakhera	70 D.G.M. (M.P.)	2-5	25-30	29-30	38-42
Umaria	48 (I.C.C. 1946)	7-10	18-20 (a few about 30)	22-29	41-53
Johilla	81 (I.C.C. 1946)	—	7-13	32-37	53-56
Sohagpur	4000 (I.C.C. 1946)	3-6	11-17 (Two samples gave over 30%)	18-30	40-63
Sonhat	94 (G.S.I. 1945)	3-6 (few 8-12)	25-35 (few 16-19)	25-30 (a few 14-22)	41-56
Jhagrakhand	66 (I.C.C. 1946)	4-9	6-23	28-34	53-57
Chirimiri	85	6-7	9-15	28-29	50-52
Kurasia	240 (G.S.I. 1945)	4-10	10-14	28-34	—
Bishrampur	235	7-11	8-12	28-35	53-57
Korba	389 (I.B.M.)	4-10	17-20 (few over 30 also)	20-32	36-44
Mand-Hasdo	Vast quantity of inferior grade coal	4-5	36-45	25-26	—
Raigarh	Estimate not available	4-7	25-27	25-26	44-46
Singrauli	785 (G.S.I. 1960)	4-9	17-22	29-31	41-44

The coke breeze may also be sold to the power station if no alternative outlet can be found for it.

Proximity to the Market. For the disposal of semicoke an easily accessible market without involving long transportation is essential.

Considering the above points, the following may be regarded as suitable places for the establishment of l.t.c. plants in Madhya Pradesh: (1) Pathakhera coalfield, (2) Amlai-Sohagpur coalfield, (3) Singrauli coalfield.

TABLE 2—GRAY-KING ASSAY OF SOME MADHYA PRADESH COALS

Name of coalfield	Yield from Gray-King assay at 600°C.			
	Coke %	Tar gal.	Liquor gal.	Gas cu. ft per ton of coal
Sohagpur (Burhar)[5]	76	21·5	16·5	2993
Singrauli (Purewa seam)[7]	73	18·71	16·52	3304

The Gray-King assay of the coal available in these places is given in Table 2.

The coalfield at Pathakhera is now being prospected. Although the samples of coal from near the outcrop have high ash content, it is hoped that the ash content will decrease towards the dip of the seams.

A thermal station of 160 MW capacity is being set up here. Sufficient water will be available from the Tawa river. The char can find good market by replacing the charcoal, provided the cost of the semicoke is lower than charcoal.

In the Sohagpur coalfield the l.t.c. plant can be located near Amali where a thermal power station of 60 MW capacity is being set up by the M.P. Electricity Board. Large quantities of suitable grade of coal are available in this coalfield which is being prospected by the Geological Survey of India. The Son river can meet the water requirements of the plant. The semicoke will find easy market in cities like Bilaspur, Raipur, Bhilai, Durg, Rourkela, Katni and Jabalpur and also Allahabad and many of the other towns lying in between.

The Singrauli coalfield is being prospected by the Geological Survey of India[7]. The coal of the Purewa seam is suitable for l.t.c. Reserves in this seam alone have been estimated to be around 385 m. tons. The coal of the Turra seam being of Grade I and low in ash content should be conserved for purposes other than l.t.c. in the interest of national economy.

A 250 MW thermal plant is being set up based on Singrauli coal but the exact location has not been decided. If it is set up near Pipra on the Rihand dam, the carbonization plant should be set up close to it and the requirements of water can then be met from the Rihand reservoir.

In the Third Five Year Plan period the National Coal Development Corporation is planning to raise 2·5 m. tons of coal per year from the Singrauli coalfield. The coalfield is being connected by rail with Robertsganj in Uttar Pradesh and a railway alignment survey is being carried out to connect the coalfield to Katni through Boohari in Shahdol district. The domestic fuel market of the thickly populated cities and towns of Uttar Pradesh and northern part of Madhya Pradesh will easily consume the semicoke produced in the plant.

Korba does not appear to be a suitable site for establishment of a l.t.c. plant, because the thick seam is too high in ash (about 40 per cent) and the Ghordewa seam has very low ash content (10-12 per cent) which can be usefully blended with coking coal from Bihar for the production of metallurgical coke.

The economic aspects of industrial carbonization plant without any tar processing plant are considered below.

It is considered that a plant processing 800 tons of coal per day is an economic unit[8]. A tentative estimate for such a plant is given below:

		Rs
I. Capital Cost—Capital investment per ton of coal carbonized per year		
(1) Machinery, apparatus, etc. carbonization plant at Rs 41 per ton	41 × 264,000 =	1,08,00,000
(2) Building, roads, etc. carbonization plant at Rs 5 per ton	5 × 264,000 =	13,00,000
	Total	1,21,00,000
II. Working Capital (3 months' working expenses, *see* below)		23,00,000
III. Cost of Production (per day)		
A. Raw Material		
(a) Coal —800 tons (including for boiler and producer gas) at Rs 30/ton	810 × 30	24,300
B. Services		
(a) Water 2 m. gal. at Rs 0·10/1000 gal.	2,000,000 × 0·10	200
(b) Power 10,000 KWh, at Rs 0·08/KWh	10,000 × 0·08	800
(c) Phenosolvan, 12 lb. at Rs 200/ton		12
C. Labour		
(a) Labour, 150 skilled and unskilled at an average wage of Rs 2·50/day	150 × 2·50	375
(b) Supervision, 40% of the labour		150
Working cost per day		25,837

		Rs.
Working cost per day		25,837
D. Indirect Cost		
(a) Maintenance at 3% of capital investment		122
(b) Depreciation at 8·3% of the same		3,043
(c) Interest overheads taxes and development at 8·5%		3,116
E. Interest on 3 months working capital (Rs 25,837 × 90 = Rs 23,25,330 or say Rs 23,00,000) at 5·5%		383
	Total	32,501
IV. Product		
Domestic coke (+1/2″) tons	520	
Coke breeze (−1/2″) tons	80	
Coal slack, tons	150	
Tar, tons	64	
V. Return		
Coke breeze −1/2″ at Rs 20/ton	80 × 20	1,600
Coal slack at Rs 20/ton	150 × 20	3,000
Tar at Rs 105/ton	64 × 105*	6,720
	Total	11,320

Cost of domestic coke per ton: Rs $\frac{32501-11320}{520}$ = Rs 40·73 nP

or Rs 41·00 nP

*As ascertained from Messrs Hindustan Steel Ltd.

This cost appears reasonable at present, in view of the fact that the selling price of charcoal at different places in Madhya Pradesh is approximately Rs 135 per long ton and that of the smokeless domestic fuel sold by Regional Research Laboratory, Hyderabad, is Rs 132 per metric ton.

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DISCUSSION

Shri K. K. Chowdhary: In the preparation of this paper, the booklet published by the Planning and Development Department of the Government of Madhya Pradesh has been consulted. The data included have been supplied by the Planning Department, Government of Madhya Pradesh and the Regional Research Laboratory, Hyderabad. Some data have also been taken from the various reports published by the Central Fuel Research Institute, Jealgora.

Shri B. S. Deshmukh: Shri S. K. Barooah and Shri K. K. Chowdhary suggested Pathakhera as one of the sites for setting up an l.t.c. plant in Madhya Pradesh. Pathakhera is still a virgin field and reserves are yet to be proved. Prospecting has just been started. It lies on the western side of Kanhan valley and coal of this area may be caking. In such case, other methods of utilizing this should be thought of, as for example, blending with metallurgical coal. The authors do not consider Korba as a possible site for l.t.c. The thick seam of 80-100 ft is of inferior quality with 40 per cent ash but occurs under a thin overburden and coal can be mined by open-cast method. If Korba coal is to be used at the power station alone, the required production will not be much and the economics of mining of small quantities will be unfavourable. On the other hand, if there is an integrated method of utilization, coal can be mined in large quantities. It is not desirable to transport high-ash coal. If it is washed, the shaly portion can be removed and the floats with 30 per cent ash will be used for power generation and domestic fuel manufacture. The +1 in. material will go for l.t.c. and −1 in. for power generation. Korba coal in view of its high exinite content will yield 18-19 gal./ton tar. Mines can then be planned for a bigger production.

Shri K. K. Chowdhary: Prospecting in Pathakhera has been started. It was found that an area of 0 9 sq. miles contained 2 seams with estimated coal reserves of 12 million tons. The prospecting is continuing. Coal from Kanhan valley has been found from the analysis of coal survey station at Nagpur to be non-caking. If Korba coal with high ash can be economically carbonized at low temperature, a plant can be installed there.

A Study of the Economics of Low Temperature Carbonization Industry in India

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Economics of production of domestic coke by low temperature carbonization of Indian coals in Lurgi-Spuelgas plants of capacities of 100-1600 tons per day is discussed (based on the pilot plant studies conducted over the past 8 years). The factors influencing the cost of production of domestic coke and the extent and type of byproduct processing that can be undertaken are considered in relation to the capacity of the carbonization plant. It is concluded that low temperature carbonization can be an economic industry. Road tar, creosote oils, tar acids and other products of satisfactory quality can be manufactured from the liquid byproducts.

The need for the establishment of low temperature carbonization (l.t.c.) industry in India for the production of smokeless domestic coke has already been discussed in earlier publications[1,2]. In South India, the domestic fuels commonly used are charcoal, firewood and animal dung cakes. Semicoke or coke was never used in this region as domestic fuel. It was therefore considered desirable, as a first step, to establish a pilot l. t. c. plant of a reasonable capacity to achieve the following objectives:

(1) To establish the suitability of locally available non-caking coals and other Indian coals for l. t. c.

(2) To familiarize the population in the region with the use of semicoke as a domestic fuel and to prepare a ready market for the product from a large-scale plant.

(3) To study various methods of economic processing of low temperature (l. t.) tar which is quite different from high temperature tar.

(4) To collect the necessary technical and socio-economic data required for the establishment of a large-scale l.t.c. and byproduct recovery industry.

(5) To train technical personnel in the operation of l. t. c. plants.

With these objectives in view, a pilot plant of the Lurgi-Spuelgas type with a throughput of 25 tons of coal per day was installed in 1953 at the Regional Research Laboratory, Hyderabad. The experience gained in the operation of this plant, the pilot scale tests conducted on different Indian coals and a study of the marketability of semicoke (which is sold under the trade name 'Kolsit') in Hyderabad and Secunderabad cities (to a small extent in Bombay also) during the past 8 years have clearly proved that the objectives with which the pilot plant was installed were largely achieved.

RESULTS OF PILOT PLANT TESTS

The results of l. t. c. tests conducted on different Indian coals have already been discussed[3,4]. The semicoke produced from various coals proved to be completely satisfactory as domestic fuel. Since the success of the l. t. c. industry, however, depends upon the proper utilization of the main byproduct, the l. t. tar, detailed investigations were taken up on the processing of tar. Processes were developed at this laboratory to prepare several products of satisfactory quality, such as road tar[5,6], creosote oil for disinfectants[7], timber creosote[8], illuminants[9] and tar acids.

The extent of processing byproducts depends mainly on the capacity of the carbonization plant and on the marketability of the products. Laboratory and field tests have proved that all the products can be marketed for direct use (e. g. road tar, timber creosote, etc.) or as raw materials for manufacture of other products (e. g. tar acids for manufacture of plastics and synthetic tannins).

ECONOMICS

Based on the pilot plant studies on production of domestic coke and on processing of byproducts, the economics of l. t. c. industry has been worked out for plants of throughput capacities of 100, 280, 400, 800 and 1,600 tons of sized coal per day. The capital investment for the plants is given in Table 1, requirements of raw materials and services in Table 2, products and returns in Table 3 and cost of production in Table 4.

The capital investment covers imported and Indian supplies. There is considerable scope for reduction of imported items which include the main carbonization, benzole recovery, Phenosolvan, tar distillation and other plants. Experience has shown that several accessory units can be manufactured in India, thus reducing the imported components. Plant costs are

TABLE 1—CAPITAL INVESTMENT FOR LOW TEMPERATURE CARBONIZATION PLANTS

	Capacity of plant (tons)				
	100	280	400	800	1600
Imported equipment (Rs millions)	1·78	3·35	4·12	11·99	22·96
Indian supplies (Rs millions)	1·59	3·10	4·05	8·55	15·68
Cost of plant as erected: (Rs millions)					
Liquid products not processed	3·37	6·45	8·17	18·54	36·64
do processed	3·67	6·95	8·97	20·54	38·64
Working capital per year: (Rs millions)					
Liquid products not processed	1·19	3·42	4·34	8·10	16·51
do processed	1·29	3·52	4·54	8·30	16·81
Cost of production per ton of domestic fuel					
(1) Singareni Coal:					
Liquid products not processed (Rs)	81·51	72·30	63·22	61·80	60·55
do processed (Rs)	77·90	67·80	58·50	54·60	53·10
(2) Jambad Coal:					
Liquid products processed (Rs)	..	..	..	40·10	38·40
(3) Ghughus Coal:					
Liquid products processed (Rs)	..	..	..	51·80	50·00

TABLE 2—REQUIREMENTS OF RAW MATERIALS, SERVICES AND LABOUR

(Yearly basis)

	Plant capacity, (tons per day)	
	800	1600
(1) Raw Material		
Coal, sized 50-150 mm. (tons)	264,000	528,000
(2) Services		
(a) Power (100 KWh)	3,630	9,240
(b) Steam at 35 p.s.i.g. (ton)	18,150	21,450
(c) Steam at 70-110 p.s.i.g. (ton)	6,600	13,200
(d) Water replacement (1000 cu.m.)	438	876
(e) Phenosolvan (tons)	12 15*	20 25*
(3) Personnel		
(a) Labour (No.)	200	300
(b) Supervisors (No.)	20	35

*This requirement is in the case of Jambad coal.

TABLE 3—PRODUCTS PER YEAR AND RETURNS

	Source of coal					
	Singareni		Jambad		Ghughus	
Capacity of plant, tons	800	1,600	800	1,600	800	1,600
Products:						
Domestic semicoke +12·7 mm., tons	158,400	316,800	144,000	288,000	131,500	263,000
Semicoke −12·7 mm., tons	26.400	52,800	17,590	35,180	28,800	57.600
Crude tar acids, tons	850	1,700	1,360	3,720	1,072	2,144
Ammonia, tons	400	800	640	1,280	340	680
Crude motor spirit, tons	1,400	2,800	2,240	4,440	2,750	5,500
Road tar, tons	6,365	12,750	10,180	20,360	7,970	15,940
Cresote oil, tons	4,243	8,486	6,788	13,576	5,347	10,694
Fuel oil, tons	1,148	2,296	1,836	3,672	1,447	2,894
Light oil, tons	80	160	128	256	100	200
Surplus gas of 200 B.t.u./cu. ft/hr, cu. ft	..	250,000	..	360,000	..	205,000
Returns on Products (Rs thousands):						
Semicoke (−12·7 mm.) @ Rs 12/ton	317	634	211	422	346	691
Crude tar acids @ Rs 500/ton	425	850	680	1,360	536	1,073
Ammonia @ Rs 500/ton	200	400	320	640	170	340
Crude motor spirit @ Rs 140/ton	196	392	314	628	385	770
Road tar @ Rs 250/ton	1,591	3,182	2,545	5,090	1,993	3,986
Cresote oil @ Rs 250/ton	1,060	2,121	1,697	3,394	1,337	2,674
Fuel oil @ Rs 112/ton	129	258	206	412	162	324
Light oil @ Rs 250/ton	20	40	32	64	25	50
Total	3,938	7,877	6,005	12,010	4,954	9,908

separately given for two cases: one including and the other excluding plants for processing liquid products.

In the case of 100, 280 and 400-ton plants, tar is processed only into road tar, creosote oil and fuel oil. Extraction of tar acids using current methods in these cases is not considered economical.

TABLE 4—COST OF PRODUCTION OF DOMESTIC COKE
(Yearly basis)

	SOURCE OF COAL					
	Singareni		Jambad		Ghughus	
Capacity of plant (tons per day)	800	1,600	800	1,600	800	1,600
A. Direct cost						
Working cost (in thousands)						
1. Raw material						
Coal @ Rs 28·05/ ton	7,405	14,810	*6,600	*13,200	*6,600	*13,200
2. Services						
(a) Power @ Re 0·09/KWH	328	832	327	832	327	832
(b) Steam 35 p.s.i.g. @ Rs 9/ton	119	193	119	193	119	193
(c) Steam 70 to 110 p.s.i.g. @ Rs 14/ton	93	185	93	185	93	185
(d) Water @ Re 0·42 per cu.m.	18	37	18	37	18	37
(e) Phenosolvan at Rs 2000/ ton	24	40	30	50	24	40
Total	7,987	16,097	7,187	14,497	7,181	14,487
3. Labour at Rs 125/month	300	450	300	450	300	450
4. Supervisor at Rs 600/month	114	264	114	264	114	264
Total direct cost	8,401	16,811	7,601	15,211	7,595	15,201
B. Indirect cost (on capital) (in thousands)						
Maintenance 3% Depreciation 8·3% Interest 5·5% Overheads 1·0% Taxes 1·0% Development 1·0% } 19·8%	4,067	7,651	4,067	7,651	4,067	7,651
Interest on 3 months working capital @ 5·5%	116	231	105	209	104	209
Total indirect cost	4,183	7,882	4,172	7,860	4,171	7,860
Total of (A+B)	12,584	24,693	11,773	23,071	11,766	23,061
C. Net cost of production of domestic semicoke	8,646	16,816	5,768	11,061	6,812	13,153
D. Cost of production per ton (Rs)	54·6	53·1	40·1	38·4	51·8	50·0
E. Cost of production with 10% profit on capital (Rs)	67·5	65·6	54·3	51·8	67·4	65·0

*Coal at Rs 25 per ton.

COST OF PRODUCTION OF DOMESTIC COKE

The cost of production of domestic semicoke (product above 1/2 in. size) from different coals has been worked out (Tables 3 and 4) assuming nominal returns for different byproducts. The estimated returns should be deemed conservative considering the present market prices and can be increased by suitable changes in the processing of byproducts. For example, the cost of production of creosote (Type I) for timber preservation is about Rs 1·50 per gallon whereas the present selling price is Rs 3·25 per gallon (approx. Rs 700 per ton); similarly, the present selling price of disinfectant creosote (white emulsion grade) is about Rs 3·50 per gallon. If pitch is manufactured, the selling price is about Rs 300 per ton. These products can be manufactured with the equipment already covered by the capital costs given in Table 1.

It is seen from Tables 1 and 4 that for a 800-ton plant the cost (ex-works) of semicoke from Andhra Pradesh coals works out to about Rs 55 per ton starting with a coal price of about Rs 28 per ton. The cost is substantially reduced as the capacity is increased from 100 to 400 tons of coal per day. For higher capacities byproduct processing makes substantial difference. The cost of the Jambad semicoke is lower due to the lower cost of Jambad coal and higher tar yields. In all the cases, plant profits, transport charges, and agent's commission should be added. These additional charges are expected to bring the sale price of semicoke to about Rs 85-100 per ton. Charcoal, against which semicoke is expected to compete, is now available in the local market at a price of Rs 150-200 per ton depending upon seasonal fluctuations. In Bombay the price of charcoal is much higher.

FACTORS INFLUENCING COST OF PRODUCTION

1. An increase of Re 1·00 per ton in the price of raw coal is expected to raise the price of semicoke by about Rs 1·75.

2. The ex-works cost of semicoke can be reduced if credits are taken for surplus gas and if the crude tar acids are further processed. In the latter case the price reduction can be Rs 3-4 per ton for a 1600-ton plant.

3. The extent of secondary processing of byproducts that can be undertaken is governed by the capacity of the carbonization plant. As the carbonization capacity is increased, the byproduct processing can also be intensified. The developments and activities of the Coalite & Chemical Co. Ltd in U. K.[10] illustrate this point.

It is seen from Table 1, that the difference between costs of production of domestic coke with and without byproduct processing, is appreciable in the case of larger plants, for example, for plants of capacities 800 and 1600 tons per day. Cost calculations for a 3200-ton plant done in 1955 (not reported here) showed that the price of semicoke would be about Rs 37 per ton. A tar hydrogenation plant to produce diesel oil and other liquid fuels could be installed as an adjunct to such a large-scale carbonization plant. The type of byproduct processing that can be undertaken, however, depends on the current market position of competitive products.

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Problems Connected with the Establishment of Low Temperature Carbonization Plants in India

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The need for developing low temperature carbonization industry in the country at the earliest is brought out. This will not only meet the demands for domestic fuel but will also form the basis for a chemical industry. In view of the complexities involved, high capital cost needed for such plants, it seems that the public sector should be the pioneers in this field.

It is widely recognized that next to food and clothing, domestic fuel is the most essential need of the people. With the rapid growth of population and industrial expansion of the country, the demand for energy has also increased. Even so, the country's energy consumption per head is still among the lowest in the world. For the purpose of cooking and heating throughout the rural and urban areas, dried cattle dung is the main source of energy. It has been estimated that the amount of cattle dung (wet) annually available is 1200 million tons of which 400 million tons are used as fuel and 215 million tons as manure, the balance being wasted. On the basis of energy content, 400 million tons of dung is equivalent to 46 million tons of coal. Fuel wood consumption of the country is estimated to be 60 million tons, which in terms of energy equivalent would equal roughly to 35 million tons of coal. Apart from cattle dung and firewood, other sources of domestic energy are the small quantity of soft coke produced in the country by the wasteful 'country-bhatta' system, coal gas, natural gas, kerosene, electricity, etc. Bottled gas has become popular with the middle or the upper middle classes in the few cities where it is available. If a comparative study is made of all these varieties of fuel, it becomes very clear that amongst the substitute fuels for dung and firewood, the cheapest is the soft coke.

NEED FOR LOW TEMPERATURE CARBONIZATION (L.T.C.) INDUSTRY

The National Council of Applied Economic Research (N.C.A.E.R.) have in their Report 'Domestic Fuels in India' compared the burning of 400 million tons of cattle dung, instead of using it as valuable natural manure as equivalent to "burning of twelve Sindris every year"[2]. Forests have a moderating influence against floods and erosion and they help in soil conservation and in maintaining soil fertility. Unfortunately the country's forest resources are very meagre; moreover, our forests are concentrated in a few States only. The burning of this forest wealth therefore presents a serious problem which must be tackled in an organized manner. People in Rajasthan are known to dig out from the already barren lands, roots and shrubs for use as domestic fuel—roots, which if left alone, might have grown into shrubs and trees and staved off the approaching deserts. For taming the deserts, ambitious schemes have been undertaken to build dams and to dig canals, as also extensive programme of afforestation, but unfortunately, little could be done so far to stop the denudation of forests by providing alternative domestic fuels at cheap rates to the users of firewood.

BYPRODUCTS OF L.T.C.

Fuels such as electricity, gas, kerosene, etc. are evidently costlier than soft coke. Even the capital investment required in installing the hot-plates, cooking range or stoves are beyond the reach of the majority of the people. Obviously, therefore, soft coke produced by means of l. t. c. of coals is the answer. There is no justification in increasing the poduction of soft coke by the existing wasteful method of stack-burning. The byproduct recovery of valuable chemicals is something which cannot be ignored. Some of the prize products of the chemical world, such as benzene, toluene, xylene, naphthalene, phenol, etc. are derived as such byproducts, besides road tar. India is deficient in kerosene supply, middle oil, diesel oil, etc. and these too can be obtained as byproducts of the l. t. c. plants.

However, with the rapidly accelerated oil production in sight, a doubt arises as to the prudence of developing the coal chemistry. Petrochemicals have a natural advantage over those produced from coal. Coal has first to be made into liquid and then converted into the desired chemical forms. Oil is already a liquid, as it comes from the ground. Chemicals made from oil are, for this and other reasons, less costly than coal chemicals. Therefore, one would ask whether considering the dwindling markets for coal chemicals, the latter face an uncertain future. Indeed, the virtue of l. t. c. of coal would just vanish if the byproduct recoveries cannot be sold or utilized. However, this question can be answered and doubts set at rest by quoting from an article "The New Look in Coking", by Mr. John B. Shallenberger, President, Connellsville Corporation, Pa. He says, "The eventual emergence of petrochemicals as a world-wide competitive winner is clear, but that is not to say that petrochemicals will be the only finalist. Market demand itself is expanding, and demand enough for all, both petrochemicals and coal chemicals is visible in at least the distant future. A look at world reserves would suggest, also for distant future, earlier depletion of petroleum resources than coal".

PRESENT AND FUTURE DEMAND FOR SEMICOKE

The other pertinent question that is raised in certain quarters is whether semicoke would be tolerated as a domestic fuel in view of the steady improvement in our standard of living. There appears to be no reason for this apprehension. By 1975, the shortage of firewood alone is anticipated to be about 100 million tons[3]. N.C.A.E.R. have recommended the l. t. c. capacity for processing 2·5 million tons of coal per year to start with to be ultimately expanded to 25 million tons per year by 1976-77[4]. These estimates should not be considered excessive considering the large population of the country. In the U.K., the Minister of Power set up a Committee under the Chairmanship of Mr N. M. Peech to inquire into the availability and suitability of solid smokeless fuels and arrangements for their distribution. The Committee in its report published in April 1960 accepted the estimates by the Ministry of Power that the annual demand for these fuels in the domestic market might increase from the current level of some 6 million tons to 115 million tons by 1965[5]. In other words, when even in the U.K. where the standard of living is much higher than that in India, it is found that the consumption of solid domestic fuel would be doubled in five years, there could be no reason or justification to assume that the demand for similar fuel in India would dwindle.

PROVISION IN THE THIRD FIVE YEAR PLAN

Obviously, therefore, l. t. c. of coals is an industry which must be developed at the earliest opportunity—not merely because of the need for domestic coke about which there is no dispute—but also because on it depends the coal chemistry so vital to the country. This country cannot go on perpetually depending on others for essential requirements of coal, based chemicals like toluene, xylene, naphthalene, phenol, etc. The southern region suffers most from the shortage of domestic fuel; however, large and extensive reserves of lignite have recently been discovered in this region. Government have sanctioned the Briquetting and Carbonization as a constituent scheme of the Integrated Neyveli Lignite Project, in which annually about 1·5 million tons of lignite will be processed by l. t. c. method to produce 3,80,000 tons of carbonized briquettes which can be used as excellent smokeless domestic fuel. This scheme would be costing about 200 million rupees. Pilot tests have shown that the carbonized briquettes are smokeless and can withstand transport over long distances without breaking up; these will be excellent substitutes for charcoal. The public sector programme of the Third Five Year Plan includes a proposal for the establishment of l. t. c. plants to process 2·2 million tons of coal for the production of soft coke. For this purpose a provision of 220 million rupees with the foreign exchange cost element of Rs 150 million has been made in the Third Five Year Plan. However, as indicated in the report "the approach to developments in this field is flexible"[6]. There being a large unbridged gap in the total proposed outlay on the plan and the financial resources in sight, Government of India have not found it possible to make financial provision for l. t. c. plants in the public sector in the Third Plan. This is a disappointment shared by all. A close watch on the resources position is being maintained, and as soon as the necessary financial resources become available, a beginning will be made of this so far neglected industry.

Meanwhile the experimental and developmental work being carried out in the various research institutions, notably the Central Fuel Research Institute (CFRI), Jealgora and the Regional Research Laboratory (RRL), Hyderabad, is being watched with interest. The research work on special methods of producing domestic coke in the CFRI is of special interest; they have experimented with different types of coal and have by now collected considerable data. The RRL has also been experimenting with its pilot plant, attaining a large measure of success, as is apparent from their product 'Kolsit'. These two premier laboratories may be aware that in recent years much of the work of the National Coal Board, U.K., has been directed towards research on the process of making a new smokeless fuel, mainly for domestic use in open grates or closed appliances. Similar research should also be extensively undertaken in this country. If this meets with success, then the country would have found a way to dispose off the large quantity of small sized coal (—25 mm.), and also to meet at least a part of the acute domestic coke shortage faced at present. If a suitable avenue to utilize small sized coal is opened up, there will be a great future for the collieries—particularly for the small collieries.

PUBLIC *Vs* PRIVATE SECTOR

There is another important question which is agitating the minds of many in the country. Now that there is no early prospect of the public sector undertaking any l. t. c. schemes in the near future, should not the private sector do something about this matter ? In 1959 the Joint Working Committee of the Coal Industry was asked to explore the possibility of some l. t. c. plants being set up by units of the private sector of coal industry and the Committee reported that "The question of setting up a low temperature carbonization plant has now been considered very carefully by each Association, Federation and by the Joint Working Committee. In view of the heavy cost of installation of the plant, it is felt that it will not be feasible for private sector companies to set up l. t. c. plants, either individually or on a co-operative basis as suggested".

Several private enterprising firms have now come forward with proposals to establish l. t. c. plants in different parts of the country. It may, however, be mentioned that there are many aspects which should be taken into account at the time of drawing up proposals for the setting up of l. t. c. plants, such as capacity of a mine or group of mines to feed the plant, etc. It would be preferable for an l. t. c. plant to be linked with a single individual mine to avoid transportation of coal by rail and assure the same source and quality of coal. Unless the entrepreneurs have control over the production of coal, the results may be disastrous. Hence the first step should be to ensure the production of coal of the correct quality and quantity.

It is clear that if this industry has to develop fully, it has to be undertaken both by the public sector as well as by the private sector.

Large number of collieries ar owned by private sector firms, and it is understandable if these firms wish to expand their present activities so as to take up the production of domestic coke and other byproducts. All present schemes and the schemes that may be taken up at a future date are, or will be, based on coal, and therefore, it would be prudent to take an overall view of the various proposals vis-a-vis the coal resources and then allow the industry to grow up in a well-planned manner and in phases.

QUALITY OF COAL AVAILABLE

In view of the acute shortage of coking coal, there can be no question of making such coal the base for the establishment of an l. t. c. plant. Even in respect of non-caking coal, care has to be taken to ensure that such of it as may be washed and made available to steel plants for use in blending, to meet at least partly the coking coal shortage, is not earmarked for any other purpose including the requirements of l. t. c. plants. That leaves us with purely noncoking coal of doubtful grades. The problems of planning and establishing an industry with an All-India coverag based upon low grade coal re far too many. For instance, when on the average only about 60 per cent of this low grade coal can be fed to the l. t. c. plants, how is one to dispose off the remaining 40 per cent slack coal ? It may be emphasized that unless the entrepreneur first makes sure about getting adequate transport not only for the manufactured product, but also for the raw material as also for the disposal of slack coal, it would be a risk for him to set up such plants. As the country will ultimately need l. t. c. coke, the Railways may consider such proposals sympathetically.

AVAILABILITY OF COAL

An important question that has to be decided in each case is whether it would be possible, with the existing coal production programme, to make available the coal for the proposed l.t.c. plants. The target for coal production during the third plan period has been fixed at 97 million tons per annum, and at the present reckoning, this figure does not include the requirements of coal for the l.t.c. plants. Even with this target, there would be a gap between the supply and demand. Paucity of financial resources, particularly shortage of foreign exchange, and a few other limitations have forced the planners to peg down the Third Plan target to a somewhat lower figure. Therefore, to earmark a part of the present coal production target for the l.t.c. plants would imply that other consumers would have to be deprived of the coal supply to that extent. Thus, the establishment of l.t.c. plants would necessitate, not only additional coal production, but also provisions for other ancillary facilities such as transport arrangement for both finished products and slack coal, supply of power and water, housing and amenities for workers, etc.

LOCATION OF THE PLANT

Another point for careful consideration is the location of the l. t. c. plants. Various authorities have discussed the question whether the plants should be located near the mines or near the consuming centres. The N.C.A.E.R. have recommended[7] that the plants should be located near the consuming centres. However, apparently this recommendation is based on the assumption that these plants would be based on superior grades of coal, as according to them 'it is inherently uneconomical to transport low grade coal (with high ash content), the only raw material for l. t. c. programme in India, over long distances'[8]. This is a view with which few will disagree; unless the coal is good, i.e. unless the ash-moisture content is not exhorbitant, there is, no virtue in transporting coal over long distances from the collieries to the carbonization plants. Another important aspect is to find an outlet for the surplus gas from these plants. Evidently piping of gas over long distances with the help of compressor stations, etc., would not be economical. Therefore, the ideal location for these plants would be in an area very near, or within, an area already served by a gas grid.

BYPRODUCTS

As mentioned earlier, coal chemicals must go hand in hand with the l.t.c. of coal. In fact, without recovery of the coal-based chemicals, there is no point in setting up l.t.c. plants. Otherwise the present wasteful method of producing soft coke by the country-bhatta method might, as well be continued.

To show how important it is to develop the chemical industry based on coal along with the l.t.c. schemes as also the importance attached to the integration of the two by some of the industrially advanced countries, the project of de la Houille may be taken as an example. The project is located not far from the mines with a power plant of 470,000 KVA capacity. Carling coking plant with an input of 3600 tons/day, ammonia plant, acetylene and styrene plant producing about 10,000 tons a year and a fertilizer plant producing ammonium nitrate are located in this area. The coking plant is working on a mixture of 65-85 per cent non-coking flame coal, 7-15 per cent coke dust and 8-22 real coking coal. In addition to this there is a nitric acid plant producing about 450 tons/day and a plant producing sulphuric acid from hydrogen sulphide. A process to make plastic glass from styrene is being developed in one of these factories. It was understood that by 1960, de la Houille had spent about Rs 8 billion since the last World War on this industry, of which Rs 3 billion were solely for the development of chemicals from coal.

CONCLUSION

L.t.c. plants are necessary for the country, and the earlier a beginning is made the better it will be. This is an industry which must be developed both by the public as well as by the private sectors, but considering the complexities involved and the high capital cost needed for such plants, it would seem that, the public sector should be the pioneers in this field.

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Importance of Development of Thermal Power in India and Utilization of Byproduct Coke Fines from Low Temperature Carbonization Plants for Power Generation

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The importance of giving priority for thermal power generation over hydro-power is discussed. Possibilities of integrating thermal power and low temperature carbonization plants are indicated. The semicoke fines can be used to generate electricity at an economic price and supply cheap and abundant power to the people in the distant corners of the country. This aspect is particularly important in view of the high targets in the Third Five Year Plan.

The development of river valley projects, the construction of several heavy industrial establishments, the expansion of railways, and the Five Year Plans have one common aim, viz. the economic uplift of the country and the common man. The economic progress of the country is dependent on the total energy spent, directly or indirectly. The energy resources of any country are limited to the extent that they can be developed from the known available sources, viz. coal, oil, natural gas, and hydro-electricity. Atomic power, at this stage, can only supplement the energy requirements to a limited extent, because of the high capital cost and shortage of technical personnel. The development of any source of energy is dependent on various other factors, such as the net power that can be continuously obtained, the flexibility of the scheme and the time required for tapping a particular source of energy. Of these, the time factor is of the greatest importance.

The *per capita* consumption of electrical energy in India is one of the lowest in the world[1]. Besides, the rate of rise in consumption is also low compared to more advanced countries[2]. Actually, India being an under-developed country, needs more rapid development of her power generation capacity.

Fortunately, India has good water resources and has an estimated potential capacity of 40 million KW of hydel power. But the development of all this hydel power capacity needs several years and a huge capital outlay[3,4]. Compared to a steam power plant, hydro-electric power station needs more capital. Besides, the hydel power-cum-irrigation projects take much longer duration for execution than the thermal power projects. Power development should therefore be linked with irrigation works only to the extent that is required from the point of additional food production, flood control and non-availability of coal or any other energy sources.

But, an analysis of the production of electrical power among various sources in India during the period 1950-61 shows[5] that, whereas in 1950, hydel power was only half that of thermal power, in 1961 it was expected that it would be twice that of thermal power, showing that the latter has been neglected without any adequate reason.

The Third Five Year Plan lays great emphasis on the large-scale development of heavy industries. This entails large quantities of power generation in a short time. Therefore, it is necessary that the present allotments in the developmental plans for hydel power may be reduced in view of the heavy costs and long periods of time involved in its development and the allocations for thermal power correspondingly increased, for achieving the rapid industrial development envisaged.

The general pattern of development of power from different sources in industrially advanced countries also indicates[2,6,7], that the greater proportion of power is generated from coal and oil than from hydel sources. Even in U.S.A., where very favourable conditions exist for hydel power, thermal power generation far exceeds the hydel power. By 1975, it is expected that in U.S.A. thermal power generated will be three times that of hydel power.

Thus, in view of the great importance of power generation in India, a planned development of all the country's energy resources—coal, lignite, petroleum and hydel power—is necessary. India fortunately has also vast resources of coal, especially low-grade coal of high-ash content and lignites, which may be used to a greater extent than now, for power generation.

A survey of the pattern of distribution of electricity among different categories of towns and villages in India during the first two Five Year Plans shows[8] that more and more power is being distributed to the smaller towns and villages. Thus electrification of rural areas and transmission of electricity to distant corners of the country is gaining importance. It is therefore necessary to decentralize power generation so that cheap power may be made available by reducing the transmission costs. From this point of view also, emphasis on thermal power generation gets added importance.

Further, if the cost of electrical energy is very high, all the developmental plans will suffer severely and also the cost of production of the commodities will increase. It is therefore of paramount importance that cheap power be made available for industries and for rural population and agriculture so that the vast majority of people who live in villages may reap the benefits of progress of the country.

It is generally taken for granted that cheap power can be made available only through hydel sources. This is not always true. The developmental costs of a hydel unit are charged on the irrigation project and this subsidy in capital cost is generally responsible for the low cost of hydel power. In a similar way if the thermal plant is also linked up with a chemical industry based on the recovery of valuable byproducts from coal and lignites as in the low temperature coal carbonization (l.t.c.) industry, this power source can compete with hydel power. Efforts should, therefore, not be unduly concentrated as at present on the development of hydel power only, but should also be directed towards the development of basic chemical industries attached to thermal schemes. Projects in U.S.A. are now being planned in this integrated manner.

The Government of India have started an integrated project at Neyveli to utilize the South Arcot lignites. In this plant it is proposed to briquette the lignite, carbonize the briquettes, recover the byproducts and make available the semicoke as domestic fuel. It is known from available data [9,10] that during the process of l.t.c. of high-ash coals from Singareni collieries or of lignite, sufficient quantity of byproduct coke fines, will be available for utilization in the thermal plants[7]. It has been estimated from pilot plant data collected at the Regional Research Laboratory, that approximately 50,000 to 60,000 tons of semicoke of 12·7 mm. size will be available annually from an l.t.c. plant of 1600 tons capacity per day. It has been shown that this semicoke could be made available at Rs 12/ton provided the cost of production of domestic coke is kept approximately Rs 50/ton. However, assuming a further rise of Rs 4/- to Rs 5/- in the price of semicoke and taking into consideration the prices of the thermal plants during the Second Five Year Plan period the cost of unit energy has been worked out as shown in Table 1 to be Rs 2·88 in a 60 megawatt power plant.

However, from a 1600 tons l.t.c. plant, one can assume that approximately 170 tons of semicoke of —12·7 mm. size will be available per day. This works out to approximately the fuel requirements needed for a 20 megawatt station with 60 per cent load factor at 570 g. of semicoke per unit energy. The semicoke could be utilized directly or as a blend up to 30 per cent along with nut coal or coal fines depending upon the type of combustion chamber.

TABLE 1—PRELIMINARY COST ESTIMATE FOR 60 MW STEAM POWER PLANT

Boiler plant, Rs	11·87	million
Turbine plant, Rs	8·53	do
Pipe work, Rs	2·67	do
Coal handling plant, Rs	0·93	do
Switchgear, Rs	2·67	do
Miscellaneous supplies, Rs	1·33	do
Total (including freight, insurance, erection at site), Rs	45·0	do
Price of low-grade fuel at pit head per ton, Rs	17	
Fuel (hard coal)/KWH, g.	575	
Coal per day, tons	600	
Coal cost/year @ Rs 17/ton, Rs	3·73	million
Cooling water, Rs	0·20	do
Boiler water, Rs	0·0525	do
Staff and labour, Rs	0·5	do
Repairs, Rs	1·8	do
Interest @ 4%, Rs	1·8	do
Depreciation, Rs	1·8	do
Capital charge, Rs	1·8	do
Total cost per year, Rs	9·08	do
Cost of energy/KWH (80% load factor)	2·88 nP	

With the modern developments in combustion technology, the efficiency of boilers has gone fairly high up to 80-84 per cent. The thermal power plant efficiency has also gone up in recent years due to improved techniques. Further, if the price of semicoke for domestic and industrial use could be increased slightly, the cost of electrical power can be reduced still further.

In the present estimates the byproduct recovery plants associated with the l.t.c. projects have been credited with returns from unprocessed crude byproducts at prices below current market levels. If, however, these byproducts are further processed and the gains from such processing diverted as a subsidy for reducing the price of semicoke and fines the price of electrical energy could be brought down still further.

In the light of recent technical advancements made possible by research in combustion and power-plant engineering, it can be confidently expected that thermal power can be produced cheaply in India, provided power plants of reasonably high capacity are located in coal-bearing areas and in places where transportation costs are not unduly high compared to the cost of coal at the mine, utilizing byproduct semicoke fines at a reasonable price.

Byproduct semicoke from l.t.c. plants and low grade coals could thus prove to be of immense value for the generation of cheap thermal power in India.

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GENERAL DISCUSSION

Dr M. G. Krishna: Shri Guha has referred to the present wasteful method of production of soft coke and stated that the virtue of l.t.c. will vanish if the byproducts recovered cannot be sold or utilized. This is an important point and should be considered with particular reference to the suggestion of Dr M. S. Iyengar to produce semicoke without byproduct recovery. To my mind, such method of l.t.c. without byproduct recovery will not be in the interests of the nation.

Secondly, the problem of slack coal has been raised and it is said that 40 per cent slack coal will be produced particularly with low rank coal. It seems to me that other methods of slack coal utilization like power generation or briquetting have to be adopted as in other countries. If the disposal of slacks is not planned in this way, it will be a problem for ever. It should not be used as an argument against the starting of l.t.c. plants based on low rank and low grade coals.

Shri Guha also mentioned the question of using 'two-fuel' processes. As I mentioned earlier in the previous session, the uneven distribution of coal reserves in the country has to be borne in mind while planning coal-based industries. I do not agree with the suggestion of the National Council of Applied Economic Research to have only plants which can produce two-fuels simultaneously. There are large resources of low-grade coal which are distributed in wide areas and if it is attempted to produce gas also, we may not succeed in all cases. The question should be left open and wherever local or economic conditions permit, single fuel processes should be considered.

While discussing the location of l.t.c. plants, Shri Guha considered that the disposal of surplus gas would be a problem if the plants are located at the coal mines and the l.t.c. plants should be installed in areas where there is already a well-laid gas grid. In my opinion, this is not a correct approach. If this is accepted as a principle, we can have l.t.c. plants only in Calcutta where there is a well-laid gas grid. Obviously, methods should be developed to utilize the surplus gas. The whole question should be kept open and depending on local conditions and distribution of coal reserves, l.t.c. plants should be based on processes which suit the coal available.

Dr S. H. Zaheer: The basic difference between our approach and that of Shri Guha and the N.C.A.E.R. is that we consider l.t.c. as also a method of upgrading and beneficiation of coal. We should think of using inferior grade coal for l.t.c. One of the parties who are likely to get a licence to put up a plant for l.t.c. have a problem in disposing their coal and getting better returns. We suggested as one of the methods, l.t.c. to manufacture semicoke for domestic purposes and liquid byproducts for further processing.

The location of these l.t.c. plants is also important. The plant either for domestic coke production alone or an integrated plant to produce gas and domestic coke should be located at the pit head. The N.C.A.E.R. has suggested locating these at the consumer points and this means using best quality coal alone as otherwise the cost of transporting high ash coal will be enormous. When the N.C.A.E.R. prepared this report, we sent our written comments thinking that they would include our comments in the final report but unfortunately this was not done. Our view is that coal which cannot be coked should be used for l.t.c. and the plant should be located at the mine. The coke should be brought to the consumer centre and if the process produces gas also, it should be piped to consumer centre.

Dr S. K. Sircar: I find, most of the authors are suffering from some kind of obsession regarding misuse of cowdung and firewood. It may be necessary to create an impression in some quarters regarding the importance of l.t.c. I do not minimize its importance, but this is not the way to do it. The problem should be considered and tackled in a different way.

The question whether coal should be used as such in a raw state or after processing is more important. If we agree that coal is to be processed before use, ways and means will have to be found as to how this can be done economically. If it cannot be done economically, the question of granting some kind of subsidy will arise. I find the cost of coke will be 1·33—2 times the price of coal. I do not agree with the entire assessment as there has been a certain amount of wishful thinking on the part of the authors which will not be actually realized. No amount of hue and cry regarding misuse of cowdung will stop the practice unless the farmer is in a position to pay the price for semicoke. In the country at present, byproduct coking industry, although well developed, cannot exist independently. This shows that there is a big difference between what can be done and what is economically possible to do.

In some papers the question of integration of l.t.c. plants has been raised. L.t.c. plant can not only be integrated with a thermal power station but also with plants requiring process steam. In the generation of thermal power, 70 per cent of heat is dissipated and only about 30 per cent of heat energy is utilized. I agree, therefore, that the l.t.c. will have to be integrated with subsidiary industry which will consume the byproducts. No such industry exists so far in the country. Even in the case of h.t.c. it has been difficult to utilize the byproducts, the uses of which have been well established. Although benzol is manufactured in the country, there is nobody to use it. We have to think well on all these aspects before drawing definite conclusions.

In the paper by Shri G. Rama Rao the economics have been carried too far. It has little relation with actual practice. It has been shown that coke breeze produced during l.t.c. can be supplied to power station at Rs 12/ton. This is subsidized coke price. The quantity of coal that has to be carbonized to produce sufficient breeze to help the thermal station going will be enormous and unless the semicoke is disposed off, it will be difficult to keep the plant going. The views expressed in the paper by Rangrez and others, are worth considering.

Regarding the paper by Dr Ratnam I wish to know as to how many will buy lignite char at Rs 150/ton.

Dr C. V. S. Ratnam: I am glad that Dr Sircar has asked about the price of lignite char. The price is much less than that of charcoal which is now commonly used as domestic fuel. We made a rough calculation and found that the quantity of semicoke of 380,000 tons per year will be sufficient to meet the demands of the cities of Madras, Madurai and Coimbatore. The present discussion is about replacing cowdung in villages and when we come to villages it may be necessary to put up one more l.t.c. plant. This present plant is intended to meet mainly urban needs.

Dr M. R. Mandlekar: We have been considering only one of the important aspects of economic utilization of various products, which could be obtained from coal. Another problem is electric power. Now that we are taking up the big task of industrialization, the generation of cheap power is a problem today. There is a general shortage of power everywhere and new industries are coming up in every part of the country. The Government of India are considering subsidizing power to the small scale industries where power rates are beyond a minimum. They are thinking of a small scale generating station to encourage establishment of industries. The question is how far this is going to meet the needs. There are various thermal power stations, diesel generating sets and hydro stations. It is a problem which we should study and suggest regarding the location of power stations. Dr Zaheer said that l.t.c. plants should be located at pit heads. At such places it might be worthwhile to locate thermal stations also and to create a grid of thermal power with hydro power.

At the same time the possibility of starting synthetic chemical industry should be considered. We should therefore, think on a long term basis and find solutions that can be placed before the government and planning commission.

Shri S. K. Nargundkar: The suggestion of Dr Mandlekar is worth considering. Integration of different industries at the coal mines is very desirable. Taking our own case of Singareni collieries, we have been asking for a power station, a fertilizer plant and an l.t.c. plant. We have waited for a number of years but slowly these are going to come one by one, because these are good suggestions. Only in the case of Neyveli lignite the planning has been done well, resulting in an integrated project. This will be an asset to the country. The question as to whether Government should start these industries or somebody else will be cleared as soon as additional resources are found. As far as local industrialists are concerned, they can make a beginning. They can start a plant in Ghughus, Talchir, Vidarbha or Pench valley. If as a result of this symposium some such plant can take shape, we should be very glad.

Dr M. S. Iyengar: Dr Sircar said that the talk about cowdung has some propaganda value. It is a fact today that out of 1200 million tons of cowdung, 400 million tons are used as fuel. This cowdung has manure value. It is true that taking advantage of the villagers we are paying only Rs 60/ton for the cowdung. It is not the real value and the value of cowdung in terms of its fertilizer component is much more. Each year by using cowdung as fuel we are burning an equivalent of 12 Sindris and it is an important national problem.

Dr Krishna referred to my remark about use of chain grate stoker for the production of domestic fuel. The ideal thing is to have a modern l.t.c. plant. Nobody disagrees with it, but nobody does it. We have been talking about this for many years. Except in Neyveli, nowhere else has anything been done. We have been burning cowdung all these years. In that connection the chain grate stoker was suggested as an expedient measure.

Dr K. L. Ramaswamy: I partly agree with Dr Sircar. Without giving a concrete proposal as to how the cowdung should be replaced by semicoke, it will be a mere propaganda. I suggest the following:

The villager will not buy soft coke since he is getting cowdung for nothing. The heat value and monetary value of cowdung and l.t. coke will have to be explained to the common man and if necessary, soft coke has to be sold at a subsidized price so that he switches over from cowdung to soft coke.

As to the price of semicoke marketed by R.R.L., I agree that the price of a product manufactured in a pilot plant cannot be compared with the actual price manufactured in industry. From the data presented, I find that a 1600 ton/day plant will be encouraging in a State like Bihar.

Dr K. Y. Shrikhande: I would like to have the cost of l.t.c. plants manufactured by Koppers and Rexco for different capacities.

Dr H. H. Koppers: The prices are available with our representative in Calcutta. The gas manufactured in our plant can not only be used as town gas but also as a synthesis gas for fertilizer, methanol and synthetic liquid fuel manufacture.

Dr M. Vahrman: The following figures are based on the plant at Edwinstowe, Nottinghamshire, England, with a yearly throughput of 220,000 tons of coal. It will be appreciated that some of the items will be substantially different in other countries.

Capitol Cost

	Per 220,000 tons of coal, £	Per ton of coal, £/sh.
Machinery, plant, railways, mechanical handling, tar storage, coal and coke screening	550,000	2·10·0
Roads, buildings, offices, laboratories	55,000	0·5·0

Running Costs

	Per ton of coal sh.
Shunting, wagon hire	1·1
Works wages, insurance, pension, holiday pay	7·4
Electricity	2·4
Water	0·1
Stores	0·6
Retort brickwork repairs (provision)	0·6
Repairs and maintenance other than brickwork	1·1
Rent, rates, schedule 'A' tax, insurance	0·8
Parent company management charge	2·2
Depreciation allowance	3·5
Advertizing	1·1
Works management and technical salaries	0·4
Office wages	0·3
Office expenditure	0·2
Research development provision	1·0
	22·8

Electricity consumption 20-21 kw per ton of coal. Water consumption 120 gal. per ton of coal.

Total Number of Operating Staff

Managerial/Technical skilled	11 (5+6)
Semi-skilled	13
Unskilled	63
Total	87

The number of skilled, managerial and technical personnel will depend, in particular, on the amount of research and development undertaken, and whether the l.t.c. is part of an integrated project, when a more economical use of such staff is possible.

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